Tuning of the Luminescence in Multiblock Alternating Copolymers. 1. Synthesis and Spectroscopy of Poly[(silanylene)thiophene]s

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ABSTRACT: Synthetic routes to alternating copolymers consisting of oligosilylene blocks and oligothiophene blocks (T_x; $x = 1, 2, 3, 4$, or 6 rings) are presented. Solubility requirements for obtaining acceptable molecular weights and, eventually, for film formation are met by the introduction of butyl groups replacing methyls on the silicon atoms and by employing T_6 blocks carrying two octyl substituents. Additionally, substituted oligothiophenes are synthesized as an aid in the interpretation of NMR, absorption, and fluorescence spectra. Regarding the electronic configuration of the oligothiophene blocks, NMR spectra show clear differences between plain oligothiophenes, end-substituted oligothiophenes, and polymers, indicative of $\pi-\sigma$ interactions with the oligosilylene blocks and possible through-conjugation to adjacent blocks in polymers. Red shifts in optical spectra show a parallel trend across the various compounds based on the same oligothiophene unit, related to the stabilization of photoexcited states on the oligothiophene by the oligosilylene substituents. These effects are strong in T_2-based compounds and reduced for longer T_n. The main feature of the spectra is the decrease of the transition energies with the size of the oligothiophene blocks in the polymers. Since this effect is also found in fluorescence, it enables one to adjust the luminescence wavelength by choosing the proper block length ("chemical tuning"). Fluorescence quantum efficiencies in solution are found to be remarkably high in polymers based on T_2 blocks. Spin-coated films of T_2-based (or T_3-based) polymers show evidence of T_4 (T_6) impurity blocks that act as an exciton trap.

1. Introduction

Polymers based on a regularly alternating arrangement of organosilicon units and oligothiophene units have raised both scientific and technological interest because of their optoelectronic properties and their apparent potential for applications as photoresists and, upon doping, as conductive materials.[1] Recent research activities in this field have shown, however, that their use as electroluminescent layer in a large-area light-emitting diode (LED) is a more promising application.

After the first report by Burroughes *et al.*[2] on diodes fabricated from poly(*p*-phenylenevinylene) (PPV), several other polymer-based LEDs were reported.[3] Soluble, processable conjugated polymers have an important advantage over inorganic semiconductors because devices can be fabricated easily *via* deposition through spin-coating on a substrate. Blue, yellow-green, and orange-red diodes have been described; these were based on homo- or copolymers with exclusively π-conjugation, e.g., poly(*p*-phenylenevinylene) (PPV), poly(3-alkylthiophene) (PAT), and poly(*p*-phenylene) (PPP). Burn *et al.*[4] reported improved efficiencies on the electroluminescence of copolymers related to PPV as a result of chemical tuning. This phenomenon was attributed to the trapping of excitons by the newly introduced, nonconjugating interrupts in a conjugated polymer. In the search for new materials for LEDs, we recently presented the realization of visible light emission from diodes made from poly[(silanylene)thiophene]s.[5] These poly[(silanylene)thiophene]s are conceptually similar to the modified PPVs with regard to the notion of exciton confinement: the oligothiophene blocks exhibit a delocalization of the π-electron density, while the oligosilylene blocks can be considered as intrinsically nonconjugated.[6] The optical properties of the polymers are therefore mainly determined by the length of the oligothiophene block. This gives us the possibility of "tuning" the luminescence of the polymers at the stage of their synthesis and enables us to make a red, green, or blue LED.

Interestingly, the behavior of poly[(silanylene)thiophene]s differs from that of PPV-related polymers. Absorption and luminescence spectra indicate that conjugation extends across the oligosilylene blocks. Several mechanisms have been proposed in relation to conjugation of some sort on silicon atoms: $\pi-d_{\mathrm{Si}}$ interaction,[7] $\pi-\sigma_{\mathrm{Si-Si}}$ hyperconjugation,[8] and the "geminal" σ-orbital overlap on silicon atoms[9] which leads to electronic band structure in polysilanes. The $\pi-\sigma$ conjugation in poly[(silanylene)thiophene]s appears to decrease with increasing length of the oligothiophene block. This could be simply considered to reflect the lowering of the energy of the π-system of the oligothiophene block with respect to the available electronic levels on the oligosilylene moiety. One should bear in mind, however, that in the context of luminescence we cannot limit our consideration to conjugation but we may have to deal with the (de)localization of excited (possibly charge transfer) and charged states. For the nondegenerate ground state π-system on hand, such "electronic defects" are predicted to be intrinsically of limited spatial extent even in the ideal, planar geometry.[10] The actual conformational disorder will reduce their delocalization still further. (The neutral and charged species are called excitons and polarons (or bipolarons), respectively. They are predicted to be accompanied by lattice deformations and introduce electronic levels within the band gap.)

In this paper we discuss several poly[(silanylene)thiophene]s, distinguished by the block lengths of the

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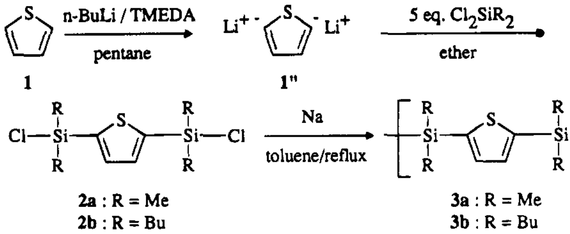
Scheme 1



oligosilylene and the oligothiophene blocks. Although we will generally refer to the organosilicon unit as "oligosilylene", in our study this block is mostly dialkylsilylene or tetraalkyldisilanylene, i.e., containing one or two silicon atoms; the "oligothiophene" (the more rigorous name being: oligothienylene) block will consist of one, two, three, four, or six thiophene rings. We present the various synthetic routes that we have followed to obtain these polymers as well as their molecular and spectroscopic characterization. In order to investigate issues of conjugation and exciton states, the spectral characteristics of each polymer will be compared with those of model compounds (referred to as "oligomers"): oligothiophenes and sil(an)yl-end-capped oligothiophenes having the same number of rings as the block in the polymer. In view of a possible application in light-emitting devices, we have prepared thin polymer films and present their spectra in this paper. In both synthesis and film formation, solubility is a key issue.

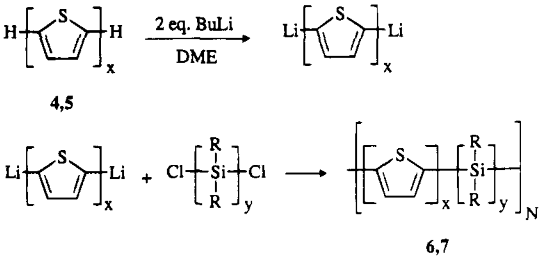
2. Synthetic Procedures

In order to find an efficient, selective synthesis for each of the polymers considered here, which differ in the number of thiophene rings and/or the number of silicon atoms in the repeat unit, several synthetic methods were explored.

Poly[2,5-(tetramethyldisilanylene)thiophene] and poly[2,5-(tetrabutyldisilanylene)thiophene] were prepared by the Wurtz coupling of the bis(chlorosilyl)-substituted thiophenes (Scheme 1). The starting monomers were prepared by adding the dilithiothiophene to an excess of the dichlorodialkylsilane. Synthesis of the monomer 2,5-bis(dimethylchlorosilyl)thiophene and the corresponding polymer has been reported by Hu and Weber[1a] and by Ohshita *et al.*,[1b] using different methods. Apart from polymers, cyclic byproducts in the polymerization were isolated in 5–10% yield. In the case of polymer **3a**, hexadecamethyloctasila[2.2.2.2](2,5)thiophenophane was isolated. This cyclic compound has already been reported by us in a previous paper as a byproduct in the reaction of the dilithio derivative of bis(2-thienyl)tetramethyldisilane with dichlorotetramethyldisilane.[6] Chicart *et al.* recently reported the formation of a series of tetrasila[1.1.1.1](2,5)thiophenophanes having various substituents.[11] The formation of these macrocyclic oligomers was shown to be dependent on the solvent used. In particular, a polar solvent such as THF gave reasonable quantities of cyclic oligomers. In our case the yield of the cyclic compound could be raised to 10–40% by applying dilute conditions, e.g., by adding the second monomer very slowly.

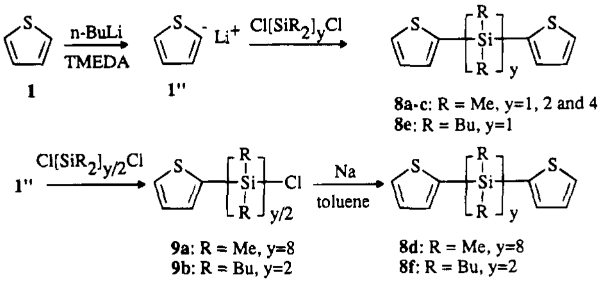
Because the synthesis of poly[(silanylene)thiophene]s via the Wurtz coupling reaction is more or less limited to polymers having single thiophene units in the backbone, owing to problems in the purification of the chlorosilyl-substituted oligothiophenes, we used a second method for polymers having bithiophene and terthiophene blocks. In our first report on the synthesis of poly[(permethylsilanylene)thiophene]s[6] we described the convenient method of the condensation reaction of dilithio derivatives of oligothiophenes with dichlorooligosilanes. This method was applied here for the synthesis of polymers **6** and **7** (Scheme 2). Direct synthesis of the dilithio derivatives of bithiophene and terthiophene was performed using the method of Chadwich and Willbe[12] as described for thiophene. Instead of hexane, ether, or THF, we used dimethoxyethane (DME) as a solvent because quenching of the dilithio derivative of terthiophene with trimethylchlorosilane showed the formation of >95% of the 5,5''-bis(trimethylsilyl)terthiophene whereas the use of THF or ether resulted in a yield of approximately 85–90% based on ^{1}H NMR spectra. GPC of the crude reaction mixtures of the polymerizations demonstrated the formation of cyclic byproducts in several cases, especially when disilanes where used. These macrocyclics were removed by precipitation in acetone or methanol or by crystallization from diethyl ether/pentane mixtures. In the case of polymer **7d**, we could isolate octabutyltetrasila[2.2]terthiophenophane and obtain good single crystals that enabled us to reveal the X-ray structure.[13]

Scheme 2



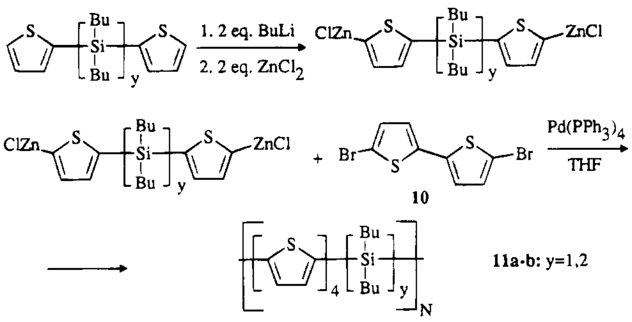
6a-b: x = 2, y = 1, 2 and R = Me
6c-d: x = 2, y = 1, 2 and R = Bu
7a-b: x = 3, y = 1, 2 and R = Me
7c-d: x = 3, y = 1, 2 and R = Bu

Scheme 3

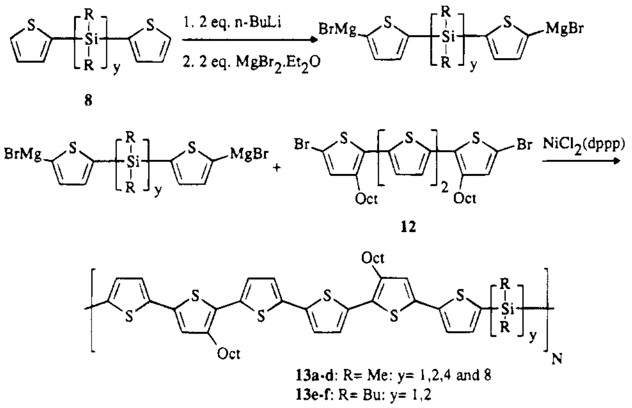


Because of the limited solubility of unsubstituted oligothiophenes longer than terthiophene, polymers with blocks of four and six thiophene units were prepared through a metal-catalyzed coupling reaction. The synthesis of the monomers **8** is described in Scheme 3. Monomers bis(2-thienyl)dimethylsilane, bis(2-thienyl)dibutylsilane, 1,2-bis(2-thienyl)tetramethyldisilane, and 1,4-bis(2-thienyl)octamethyltetrasilane were prepared by the reaction of 2-lithiothiophene with the respective dichlorooligosilanes. Dithienyloligosilanes were converted in two steps to the zinc derivatives. The poly[(silanylene)tetrathiophene]s were prepared by a palladium-catalyzed polycondensation reaction of 5,5'-dibromo-2,2'-bithiophene with these zinc derivatives[14] (Scheme 4). The resulting molecular weights are very low. This is partly due to the limited solubility of the polymers formed under the conditions used but also because conversion of the dilithio derivatives into the zinc derivatives is not quantitative and the monoderivative acts as a chain stopper. A third drawback of this

Scheme 4



Scheme 5



method is the need to use reaction temperatures of 50 °C or higher; under this condition the palladium catalyst slowly degrades.

Poly[(silanylene)hexathiophene]s were synthesized by a nickel-catalyzed Grignard cross-coupling as depicted in Scheme 5. This transition metal promoted polymerization procedure developed by Tamao *et al.*[15] for aryl bromides and first described for polymers by Yamamoto *et al.* for the synthesis of poly(phenylene)[16] and polythiophenes[17] gave polymers in good yield with reasonable molecular weights. Monomer **12** was prepared from 3,3‴-di-*n*-octylquaterthiophene by bromination with 2 equiv of *N*-bromosuccinimide. 3,3‴-Di-*n*-octylquaterthiophene was prepared by a nickel-catalyzed Grignard coupling analogous to the method used by Van Pham *et al.*[18,19] for the synthesis of methyl-substituted oligothiophenes. Octyl substituents on the quaterthiophene were chosen because of solubility. Substitution was limited to two alkyl groups which were placed on nonadjacent thiophene rings. This particular synthesis was chosen in order to avoid head-to-head substituent configurations, which would affect the interring rotation barriers and result in a blue shift of absorption maxima.[20]

3. Results

3.1. Solubility and Molecular Weight of the Copolymers. The solubility of poly[(silanylene)thiophene]s is dependent on the size and solubility of both the oligothiophene and oligosilylene units and therefore on the size of the alkyl substituents on these. The polymers in which methyl-substituted silanylene units are combined with bithiophene and terthiophene blocks were found to be crystalline; they were appreciably soluble only in thiophene and $CHCl_3$. For these polymers, it was not possible to obtain good-quality films through spin-coating. More soluble and processable polymers have been obtained by starting from silylene units with longer, flexible alkyl side groups. The use of butyl groups reduced the degree of crystallinity and resulted in sufficiently enhanced solubility for spin-coating to be feasible. As a consequence of the rather low molecular weights, relatively highly concentrated starting solutions of 1–5 wt % were required. Polymers having dibutylsilylene units are soluble in solvents such as CH_2Cl_2, THF, ether, toluene, and *n*-hexane. This has enabled us to prepare thin transparent films and obtain solid-state spectra, in addition to the solution spectra.

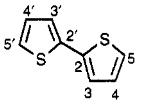
The results of the molecular weight measurements by means of gel permeation chromatography of solutions of the polymers in $CHCl_3$, and calculated relative to polystyrene standards, are listed in Table 1. The molecular weight distributions of the copolymers were generally monomodal after removal of possible cyclics for some copolymers. The observed dispersity in the copolymer samples varies from 1.3 to 2.4. The estimated degree of polymerization of about 5 for, e.g., p-$T_4Si_2Bu_4$ (**11b**), although low, still implies an average of about 20 thiophene rings in the main chain. For the copolymers **11a**, **11b**, **13e**, and **13f**, elemental analysis showed the presence of bromine in amounts of 2–3%. If one assumes that one bromine-containing end group is present, the calculated and measured elemental analytical data of C, H, S, and Br for these copolymers are in good agreement with each other.

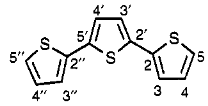
Table 1. Properties of Poly[(silanylene)thiophene]s

polymer	M_n[a]	M_w/M_n	n	mp, °C[b]	T_g, °C[b]	appearance
p-$TSiMe_2$	4350	1.4	30	120–130	21	white powder
p-TSi_2Me_4 (**3a**)	3200	1.6	16	155–165	15	white powder
p-TSi_2Bu_4 (**3b**)	2000	1.6	5		−53	white viscous solid
p-T_2SiMe_2 (**6a**)	2000	1.4	9	180–200	45	white powder
p-$T_2Si_2Me_4$ (**6b**)	2600	1.3	9	190–200	45	white powder
p-T_2SiBu_2 (**6c**)	2300	2.0	8		−10	yellow-green sticky gum
p-$T_2Si_2Bu_4$ (**6d**)	3400	2.3	8		−20	yellow gum
p-T_3SiMe_2 (**7a**)	3200	1.4	11	200–215	45	yellow powder
p-$T_3Si_2Me_4$ (**7b**)	4500	1.5	13	180–210	45	yellow powder
p-T_3SiBu_2 (**7c**)	5000	1.6	13		30	brown brittle solid
p-$T_3Si_2Bu_4$ (**7d**)	6800	2.1	13		−5	brown gum
p-T_4SiBu_2 (**11a**)	2100	1.5	5		1	orange-red solid
p-$T_4Si_2Bu_4$ (**11b**)	2800	1.6	5		−1	orange-red sticky solid
p-$T_6Oct_2SiMe_2$ (**13a**)	6000	2.4	8	50–60	31	dark red powder
p-$T_6Oct_2Si_2Me_4$ (**13b**)	9400	1.7	12	45–55	12	orange-red powder
p-$T_6Oct_2Si_4Me_8$ (**13c**)	6000	1.7	6	50–55	6	orange-red powder
p-$T_6Oct_2Si_8Me_{16}$ (**13d**)	12500	2.1	13	50–55	13	orange-red powder
p-$T_6Oct_2SiBu_2$ (**13e**)	4300	2.4	5		−1	red sticky solid
p-$T_6Oct_2Si_2Bu_4$ (**13f**)	5900	2.4	6		−10	red gum

[a] GPC, relative to polystyrene standards. [b] From DSC measurements.

Table 2. NMR Data of Selected "Model Compounds" and Poly[(silanylene)thiophene]s

	^{1}H δ, ppm		^{13}C δ, ppm				^{29}Si δ, ppm	
			C−H		C			
compound	4/4′	3/3′	4/4′	3/3′	5/5′	2/2′	$SiMe_3$	$SiMe_2$
T_2 (**4**)	7.03	7.19	127.6	123.6	124.2	137.2		
$Me_3SiT_2SiMe_3$ (**14a**)	7.13	7.23	134.6	125.0	139.6	142.4	−6.6	
p-T_2SiMe_2 (**6a**)	7.21	7.25	136.2	125.5	136.9	143.3		−15.3
p-T_2SiBu_2 (**6c**)	7.21	7.28	136.8	125.3	135.0	143.2		−13.0
$Me_5Si_2T_2Si_2Me_5$ (**14b**)	7.07	7.24	134.7	124.9	138.5	142.2	−19.2	−24.0
p-$T_2Si_2Me_4$ (**6b**)	7.05	7.22	135.3	125.3	137.4	142.8		−24.5
p-$T_2Si_2Bu_4$ (**6d**)	7.03	7.25	135.9	125.1	136.0	142.6		−21.1

	^{1}H δ, ppm			^{13}C δ, ppm						^{29}Si δ, ppm	
				C−H			C δ, ppm				
compound	4/4″	3/3″	3′/4′	4/4″	3/3″	3′/4′	5/5″	2/2″	2′/5′	$SiMe_3$	$SiMe_2$
T_3 (**5**)	7.08	7.18	7.09	127.7	123.5	124.1	124.3	136.9	136.0		
$Me_3SiT_3SiMe_3$ (**15a**)	7.13	7.22	7.08	134.7	124.8	124.3	139.8	142.1	136.2	−6.4	
p-T_3SiMe_2 (**7a**)	7.23	7.23	7.09	136.3	125.1	124.7	136.7	143.3	136.8		−15.2
p-T_3SiBu_2 (**7c**)	7.23	7.26	7.11	136.9	124.9	124.7	134.9	143.2	136.2		−13.1
$Me_5Si_2T_3Si_2Me_5$ (**15b**)	7.08	7.23	7.085	134.7	124.8	124.2	139.0	142.1	136.8	−19.2	−23.9
p-$T_3Si_2Me_4$ (**7b**)	7.05	7.21	7.07	135.3	125.0	124.4	137.6	142.5	136.2		−24.4
p-$T_3Si_2Bu_4$ (**7d**)	7.04	7.22	7.08	135.9	124.9	124.3	136.3[a]	142.2	136.2[a]		−21.1

[a] Tentative assignments.

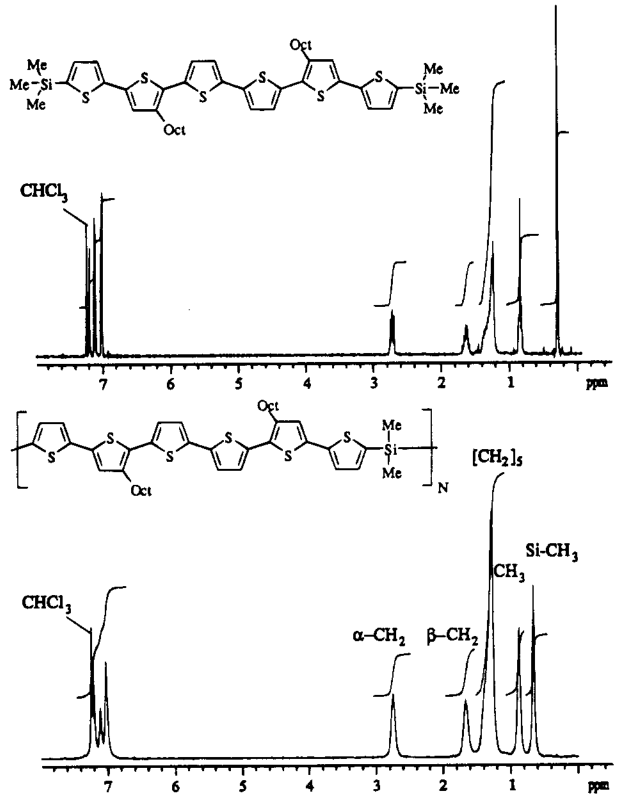


Figure 1. 300 MHz ^{1}H NMR spectra of p-$T_6Oct_2SiMe_2$ (**13a**; bottom) and of one of the related model compounds, $Me_3SiT_6Oct_2SiMe_3$ (top); both were measured in $CDCl_3$ at 30 °C.

Thermal properties and other physical data of the polymers are also contained in Table 1. The glass transition temperatures and melting temperatures listed are the results of DSC investigations. The color of the polymers obtained varied from colorless through yellow to dark red.

3.2. NMR Spectroscopy Characterization. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were obtained in $CDCl_3$. All chemical shift values are referenced to tetramethylsilane (TMS, 0 ppm). The chemical shifts of copolymers having bithiophene (T_2) or terthiophene (T_3) units and those of the corresponding oligothiophenes and some illustrative derivatives are compiled in Table 2. Chemical shift assignments for each of the copolymers were made on the basis of assignments for model compounds, e.g., T_2SiMe_3, $Me_3SiT_2SiMe_3$, T_3SiMe_3, and $Me_3SiT_3SiMe_3$. For the latter, assignments were made using a combination of techniques such as $^{1}H-^{13}C$ HETCOR, proton-coupled ^{13}C, and the relative signal intensities of the aromatic protons from the ^{1}H NMR spectra. The assignments show a high degree of internal consistency and fully confirm the copolymer structure.

The ^{1}H NMR spectra of the polymers are slightly different from those of sil(an)yl-end-capped oligothiophenes. In Figure 1 the ^{1}H spectra of polymer **13a** and its model $Me_3SiT_6Oct_2SiMe_3$ are shown. Chemical shift positions are almost identical. The resonances of the copolymer are broadened and coupling constants cannot be observed.

For several polymers some weak signals appear in the aromatic region which can be assigned to end groups. Figure 2 represents the aromatic region of the ^{13}C spectrum of p-$T_3Si_2Bu_4$ (**7d**). It clearly shows the presence of the terthiophene end groups. The assignments of the aromatic carbons of the end groups is based on a comparison of the aromatic region of the polymer with that of the model compound $T_3Si_2Bu_4T_3$ (inset). The ^{13}C spectra of the other copolymers are similar and show the presence of end groups in quantities depending on the molecular weights.

3.3. Optical Properties of Polymers and Related Oligomers. UV−vis Absorption Spectroscopy. Figure 3 shows the UV−vis spectra of a series of poly[(tetrabutyldisilanylene)thiophene]s, both in solution and as a thin film, and of their corresponding oligothiophenes in hexane. The absorption spectra of the copolymers and the oligothiophenes have similar features: one broad main peak and a shoulder at the low-energy (long wavelength) side. The absorption maxima shift to lower energies with increasing length of the oligothiophene unit. The spectra of the solid films are very similar to the solution spectra but increasingly red-shifted with respect to the latter; for the polymers with blocks of four and six thiophene rings, the red shift of the main

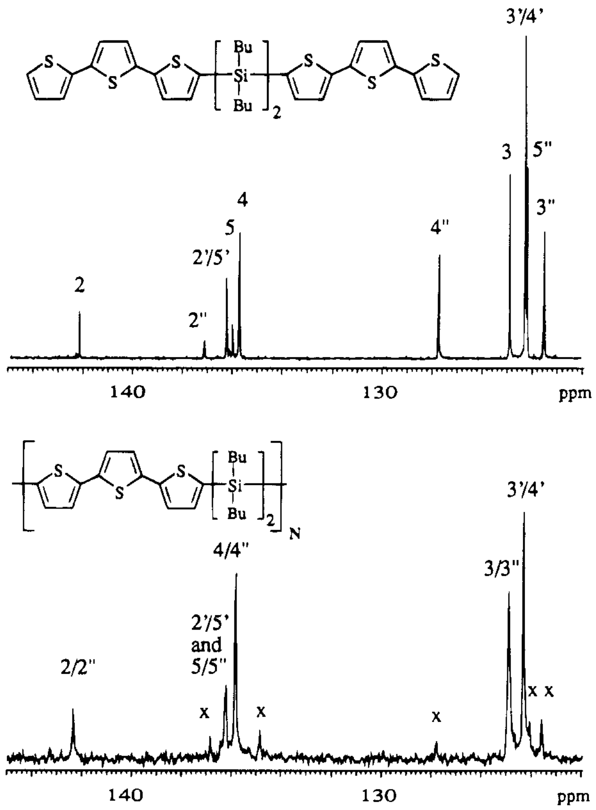


Figure 2. Enlarged view of the aromatic region of the ^{13}C NMR spectrum of p-$T_3Si_2Bu_4$ (**7d**; bottom), in $CDCl_3$ at 30 °C; for comparison purposes, the spectrum of a related model compound, $T_3Si_2Bu_4T_3$, is shown (top). The peaks corresponding to end groups in the polymer are indicated by crosses.

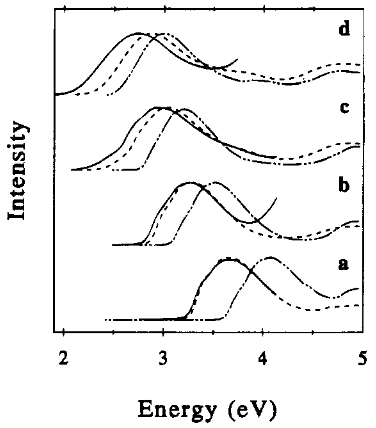


Figure 3. UV–vis absorption spectra of polymers of the general structure p-$T_xSi_2Bu_4$ in *n*-hexane solution (- - -) and thin film (—) and of the corresponding oligothiophene T_x in *n*-hexane (– - -): (a) $x = 2$; (b) $x = 3$; (c) $x = 4$; (d) $x = 6$.

maximum amounts to 13 and 39 nm, respectively. The λ_{max} values of the solutions of all polymers are given in Table 3A. For comparison purposes, the λ_{max} values of the related oligothiophenes and trimethylsilyl- and pentamethyldisilanyl-end-capped oligothiophenes are given in Table 3B. The values for the thin films of the well soluble polymers are given in Table 3C.

Fluorescence Spectroscopy. The copolymers show an intense fluorescence in solution and in the solid state. In a fashion similar to the absorption spectra, the fluorescence bands shift to lower energies with increasing length of the oligothiophene unit. The color of the emitted light varies from blue to orange in solution and from blue-green to orange-red in thin films. Figure 4 shows the fluorescence of a series of poly[(tetrabutyldisilanylene)thiophene]s in hexane and as thin films and that of their corresponding oligothiophenes in solution. The solution spectrum of a polymer is generally different from its solid-state spectrum. In contrast to the case of absorption, almost all the fluorescence bands are structured. Fluorescence maxima, fluorescence quantum yields, and Stokes shifts of the polymers in solution are given in Table 3A. Table 3B contains the data for the related oligomers and model compounds. The emissive properties of the thin-film polymers are given in Table 3C.

4. Discussion

4.1. Synthetic Routes. Different routes for achieving a selective synthesis of copolymers having thiophene block lengths of one to six rings and blocks of one to eight silylene units in the main chain were employed. The Wurtz coupling route and the polycondensation route gave as side products low yields of cyclic compounds. The presence of cyclic oligomers is a general phenomenon in the synthesis of polysilanes.[9] The Wurtz coupling of the 2,5-bis(dialkylchlorosilyl)thiophenes gave copolymers with low to reasonable molecular weights. We could not isolate any high molecular weight fractions as is described for polyalkylsilanes.

Although the use of dimethoxyethane as a solvent for the polycondensation of the copolymers **6** and **7** improved molecular weights, overall molecular weights are still low. Small quantities of the monolithio derivative of bi- and terthiophene, respectively, act as chain stoppers. In the case of the copolymers **6a,b** and **7a,b**, which have methyl substituents, the limited solubility of the polymers under polymerization conditions also affects the molecular weight. Also for the copolymers p-$T_4Si_yBu_{2y}$ precipitation of a red product was observed during polymerization. Even the presence of butyl substituents at the silicon unit apparently does not compensate for the very poor solubility of the T_4 units. In order to increase molecular weights or to efficiently copolymerize longer oligothiophene blocks, one has to start from alkyl-substituted oligothiophene units.

4.2. NMR Spectroscopy. Chemical shifts are important parameters in high-resolution NMR studies of oligomers and polymers. Apart from being the fingerprint of the primary chemical structure of the molecule under consideration, chemical shifts are also useful as a means of probing the secondary and higher order structure. The chemical shift is the parameter that characterizes the magnetic environment of the nucleus considered. The magnetic environment of a nucleus is determined by the total electromagnetic structure of the molecule, which includes nuclear magnetic moments and the distribution of electrons. Organosilyl and polysilanyl groups exert an electron-releasing inductive effect (+I effect) toward aromatic rings and an electron-attracting effect (−T effect) by $\pi-\sigma^*$ backbonding.[21] In addition, polysilanyl substituents can donate electron density toward aromatic rings by $\sigma-\pi$ hyperconjugation[8,22] from the Si−Si bonding orbitals.

The pattern of NMR spectra of the oligothiophenes and the polymers is mainly determined by the electronic effects of the sil(an)yl substituent (for selected copolymers, see Table 2). The ^{13}C chemical shifts δ of the silyloligothiophenes show an obvious increase with respect to the δ values of the unsubstituted oligothiophenes. The strong acceptor effect exceeds the inductive effect and the δ values of all carbon nuclei are shifted toward low field compared to the respective oligo-

Table 3

A. Absorption and Fluorescence Characteristics of Poly[(silanylene)thiophene]s in Solution[a]

	absorption			fluorescence				
compound	λ_{max}, nm	E_{max}, eV	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	E_{max}, eV	ϕ_F	Stokes shift, eV	E_{0-0}, eV
p-$TSiMe_2$	252[b]	4.92[b]	12300[b]					
p-TSi_2Me_4 (**3a**)	270	4.59	9300	350	3.54	≤0.01	1.05	4.13
p-TSi_2Bu_4 (**3b**)	274	4.52	9400	354	3.50	0.09	1.02	4.10
p-T_2SiMe_2 (**6a**)	326[b]	3.80[b]	*c*	371/*387*[b]	3.34/3.20[b]	0.24[b]	0.46/0.60	3.45
p-$T_2Si_2Me_4$ (**6b**)	331[b]	3.75[b]	*c*	384/*400*[b]	3.22/3.10[b]	0.58[b]	0.60/0.72	3.37
p-T_2SiBu_2 (**6c**)	330	3.75	22400	369/*384*	3.36/3.22	0.22	0.39/0.53	3.47
p-$T_2Si_2Bu_4$ (**6d**)	342	3.63	35300	380/*399*	3.26/3.10	0.44	0.37/0.53	3.35
p-T_3SiMe_2 (**7a**)	370[b]	3.35[b]	*c*	426/452[b]	2.91/2.74[b]	0.09[b]	0.44/0.61	3.00
p-$T_3Si_2Me_4$ (**7b**)	379[b]	3.27[b]	*c*	434/459[b]	2.86/2.70[b]	0.07[b]	0.47/0.63	2.95
p-T_3SiBu_2 (**7c**)	376	3.30	32800	422/448	2.94/2.76	0.14	0.36/0.54	2.95
p-$T_3Si_2Bu_4$ (**7d**)	375	3.31	38300	432/450	2.87/2.76	0.09	0.44/0.55	2.96
p-T_4SiBu_2 (**11a**)	412	3.01	24100	512	2.42	0.32	0.59	2.64
p-$T_4Si_2Bu_4$ (**11b**)	410	3.03	33200	515	2.41	0.26	0.62	2.63
p-$T_6Oct_2SiMe_2$ (**13a**)	415	2.99	45400	517/549	2.40/2.26	0.27	0.59/0.73	2.55
p-$T_6Oct_2Si_2Me_4$ (**13b**)	423	2.93	44300	517/551	2.40/2.25	0.22	0.53/0.68	2.54
p-$T_6Oct_2Si_4Me_8$ (**13c**)	424	2.93	38500	548	2.26	0.18	0.67	2.54
p-$T_6Oct_2Si_8Me_{16}$ (**13d**)	424	2.93	46200	521/*551*	2.38/2.25	0.19	0.55/0.68	2.52
p-$T_6Oct_2SiBu_2$ (**13e**)	422	2.92	40700	517/547	2.40/2.27	0.25	0.48/0.65	2.54
p-$T_6Oct_2Si_2Bu_4$ (**13f**)	431	2.87	39300	518/555	2.39/2.23	0.23	0.48/0.64	2.50

B. Absorption and Fluorescence Characteristics of "Model Compounds" in Solution[a]

	absorption			fluorescence				
compound	λ_{max}, nm	E_{max}, eV	ϵ, M^{-1} cm^{-1}	λ_{max}, nm	E_{max}, eV	ϕ_F	Stokes shift, eV	E_{0-0}, eV[d]
T (**1**)	231	5.37	5600					5.02
$TSiMe_3$[e]	234	5.30	9200					4.79 (0.23)
TSi_2Me_5[e]	242	5.12	13300					4.66 (0.36)
TSi_4Me_9[e]	239/258	5.19/4.81	18000					4.46 (0.56)
$Me_3SiTSiMe_3$[e]	243	5.10	8800					4.64 (0.38)
$Me_5Si_2TSi_2Me_5$[e]	260	4.77	14700					4.32 (0.70)
$Me_9Si_4TSi_4Me_9$[e]	239/272	5.19/4.56	20000					4.12 (0.90)
T_2 (**4**)	301	4.12	12200	360	3.44	0.01	0.68	3.68/3.68[f,g]
T_2SiMe_3[e]	309	4.01	13200	368	3.37	0.03	0.64	3.62 (0.06)
$T_2Si_2Me_5$[e]	314	3.95	15300	374	3.31	0.05	0.64	3.57 (0.11)
$Me_3SiT_2SiMe_3$ (**14a**)	316	3.92	11800	374	3.31	0.06	0.61	3.55 (0.13)
$Me_5Si_2T_2Si_2Me_5$ (**14b**)	325	3.82	21300	390	3.18	0.23	0.64	3.46 (0.22)
T_3 (**5**)	351	3.53	23100	423	2.93	0.07	0.60	3.17/3.11[f,g]
T_3SiMe_3[e]	358	3.46	11300	413/433	3.00/2.86	0.10	0.46/0.60	3.12 (0.05)
$T_3Si_2Me_5$[e]	360	3.44	22900	416/438	2.98/2.83	0.10	0.46/0.61	3.09 (0.08)
$Me_3SiT_3SiMe_3$ (**15a**)	362	3.42	12200	418/440	2.97/2.82	0.10	0.45/0.60	3.07 (0.10)
$Me_5Si_2T_3Si_2Me_5$ (**15b**)	368	3.37	29000	424/450	2.92/2.76	0.12	0.45/0.61	3.02 (0.15)
T_4[g]	385	3.22	32000	444/472	2.79/2.62	0.20	0.43/0.60	2.84/2.82[f]
T_6[f,g]	432	2.87	23100	508/541	2.44/2.29	0.32	0.43/0.58	2.52
T_6Oct_2[h]	412	3.01	42600	503/536	2.47/2.32	0.29	0.53/0.69	2.58 (−0.06)
$Me_3SiT_6Oct_2SiMe_3$[h]	416	2.98	41000	510/544	2.43/2.28	0.25	0.55/0.70	2.56 (−0.04)

C. Absorption and Fluorescence Characteristics of Poly[(perbutylsilanylene)thiophene] Thin Films

	absorption		fluorescence			
compound	λ_{max}, nm	E_{max}, eV	λ_{max}, nm	E_{max}, eV	Stokes shift, eV	E_{0-0}, eV
p-TSi_2Bu_4	244/282	4.40	*i*	*i*		
p-T_2SiBu_2	326	3.80	*391*/469/501	*3.17*/2.64/2.48	*0.63*/1.16/1.32	3.35
p-$T_2Si_2Bu_4$	339	3.66	*413*/460/503	*3.00*/2.70/2.47	*0.66*/0.94/1.19	3.26
p-T_3SiBu_2	389	3.19	437/461/*522*	2.84/2.69/*2.38*	0.35/0.60/*0.81*	2.88
p-$T_3Si_2Bu_4$	391	3.17	444/470/*528*	2.79/2.64/*2.34*	0.48/0.53/*0.83*	2.87
p-T_4SiBu_2	425	2.92	*575*/618	*2.18*/2.01	*0.74*/0.91	2.38
p-$T_4Si_2Bu_4$	423	2.93	*573*/620	*2.17*/2.00	*0.76*/0.93	2.37
p-$T_6Oct_2SiBu_2$	450	2.76	640	1.93	0.83	2.29
p-$T_6Oct_2Si_2Bu_4$	470	2.64	650	1.91	0.73	2.21

[a] *n*-Hexane unless stated otherwise; ϕ_F = fluorescence quantum yield; E_{0-0} was taken as the crossing point of the absorption and the fluorescence spectra. Italicized λ_{max} values are the main maxima. [b] CH_2Cl_2. [c] Solubility < 100%. [d] In parentheses is the difference $\Delta(E_{0-0})$ of the compound with respect to the corresponding oligothiophene. [e] Full details of the synthesis and characterization will be published. [f] Garcia et al. *J. Phys. Chem.* **1993**, *97*, 513. [g] CH_2Cl_2. [h] Reference 19. [i] No fluorescence was observed.

thiophene. There is a small difference between a trimethylsilyl group and a pentamethyldisilanyl group, which is most clearly seen for the (*ipso*) carbons at the 5/5′ and 5/5″ positions, respectively, which are strongly deshielded in comparison to the plain oligomer. Disilanyl end caps appear to be a somewhat weaker acceptor since deshielding is reduced in going from $-SiMe_3$ to $-Si_2Me_5$, and an upfield shift of approximately 0.9 ppm results. The other carbon nuclei are much less affected by the substitution, the order of the shift with respect to the plain oligothiophene being 5/5′ > 4/4′ > 2/2′ > 3/3′ for T_2 and 5/5″ > 4/4″ > 2/2″ > 3/3″ > 2′/5′ ≈ 3′/4′ for T_3. For T_3 only the outer rings show appreciable changes upon substitution. A similar response toward silyl substitution has been described for phenyl systems.[23]

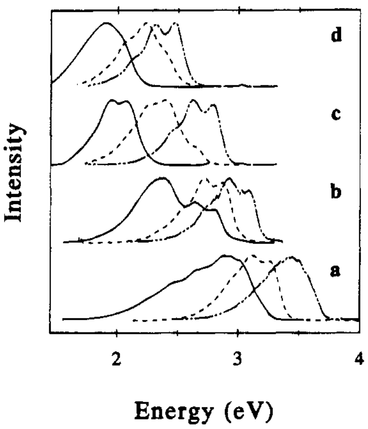


Figure 4. Fluorescence spectra of polymers of the general structure p-$T_xSi_2Bu_4$ in *n*-hexane solution (- - -) and thin film (—) and of the corresponding oligothiophene T_x in *n*-hexane (– - -): (a) $x = 2$; (b) $x = 3$; (c) $x = 4$; (d) $x = 6$.

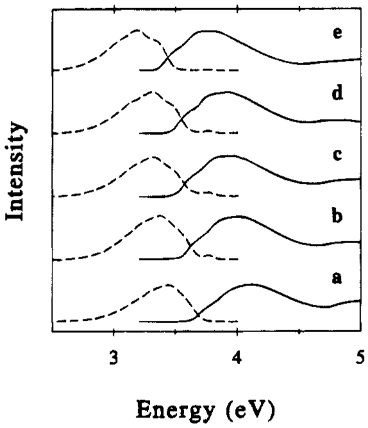


Figure 5. Comparison of UV–vis absorption (—) and fluorescence (- - -) spectra of 2,2′-bithiophene (T_2) and sil(an)yl-substituted compounds derived from T_2, demonstrating the effect of $\pi-\sigma$ interaction on E_{0-0}, the energy of the electronic 0–0 transition, which is approximated by the energy value at which the spectra intersect, as indicated: (a) T_2; (b) T_2SiMe_3; (c) $T_2Si_2Me_5$; (d) $Me_3SiT_2SiMe_3$; (e) $Me_5Si_2T_2Si_2Me_5$.

Copolymers show similar trends but there are also some differences. Again, the carbon nuclei of the oligothiophene unit next to the silylene group show the strongest deshielding effect in comparison with the simple oligothiophene. While it is systematically smaller than in the end-capped oligomers for the *ipso* carbons, deshielding at the other carbons is somewhat enhanced; the overall order is nonetheless the same as for the end-capped oligomers. Lengthening of the sil(an)ylene block of the polymer has a pronounced effect on several carbon nuclei of the oligothiophene blocks. The *ipso* C atoms, i.e., those having a direct link to the sil(an)ylene group, are deshielded approximately 1 ppm in going from one to two silicon atoms. The *ipso* carbon nuclei of the polymers therefore respond differently (enhanced deshielding) to the lengthening of the sil(an)yl(ene) unit than those of the end-capped oligomers (reduced deshielding). Another result of changing silylene to disilanylene in the polymer is the reduction in deshielding of the *ortho* and the *para* carbons, while similar effects are absent in the model compounds. These differences between polymer and model compounds reflect the completely different substitution patterns on the silicon atoms, e.g., the presence of a π system at both ends of the block in the case of the polymers.

Butylated sil(an)ylene groups are less electron-accepting than methylated ones; this is obvious from both the ^{13}C and the ^{29}Si chemical shifts. In ^{13}C it shows up in the δ values of the *ipso* carbon nuclei and, to a much lesser extent, in the δ values of the *para* (2/2′ and 2/2″) carbons; the *ortho* (4/4′ and 4/4″) carbons exhibit a small downfield effect. The stronger inductive effect of the butyl groups compared to methyls is probably the explanation for the effect on the *ipso* and *para* carbon atoms, and the deshielding on the *ortho* carbon atoms is possibly caused by direct steric effects.

The general picture that emerges here is that the polymer has the effect of the sil(an)yl(ene) moiety more spread out across the oligothiophene unit than the model compounds do, which we tentatively relate to the notion of $\pi-\sigma$ conjugation.

4.3. Optical Properties. UV–vis Absorption Spectroscopy. The comparison of a polymer and its corresponding oligothiophene shows that there is a difference in the onset of the absorption band as well as in the position of the maximum (Figure 3); the polymer spectrum is red-shifted. We attribute this to $\pi-\sigma$ conjugation across the oligosilylene blocks, which allows the conjugation length to be larger than the length of the oligothiophene block or even larger than that of the repeat unit. That the $\pi-\sigma$ interaction may extend across repeat units in the case of the polymer is supported by the spectra of sil(an)yl-end-capped oligothiophenes, which take intermediate positions between oligothiophene and polymer, as is shown in Figure 5 for T_2 blocks. Our use of the notion of conjugation length implies the assumption that the absorption of a photon excites an electron into an empty level of the "conduction band", i.e., a highly delocalized LUMO (lower unoccupied molecular orbital), rather than directly into a level within the band gap which is coupled to lattice deformations, as referred to in the Introduction. The relaxed "exciton" state is probably only relevant to fluorescence, but this is still a matter of debate.[24]

The replacement of the hydrogens at the terminal α-carbon atoms by peralkylsil(an)yl groups is expected to affect the energy of the excited state, since the electronic configuration at the terminal carbons is characteristic of this state. The excited state wave function imposes the character of the LUMO on the oligothiophene block, which results in a quinoid bonding pattern extending over a few rings.[10] For short oligomers (T_2, T_3) this state is resonance stabilized by charge-separated and biradical configurations and lends reactivity to the terminal α carbons, which acquire some radical character. Peralkylsil(an)yl groups are claimed to be both electron-donating (through the $Si-C_{Ar}$ σ bond and, in the case of silanyl groups, through hyperconjugation between the π system and the σ_{Si-Si} bond) and electron-accepting (through interaction of the π system with empty *d* levels on Si and especially with the antibonding σ^* level in silanyl groups) and may stabilize the excited state through (hyper)conjugation or through limited charge transfer. (Our own MO calculations, performed at the noncorrelated level, indicate that the addition of a silyl group to a thiophene or bithiophene system results in a lowering of the energies of both HOMO and LUMO but that stabilization is stronger for the LUMO level.) The spectra of the model compounds demonstrate that disilanyl end groups have a stronger stabilizing interaction than silyl groups, but silyl substitution at both ends of the oligothiophene block is slightly more effective than a single disilanyl group at

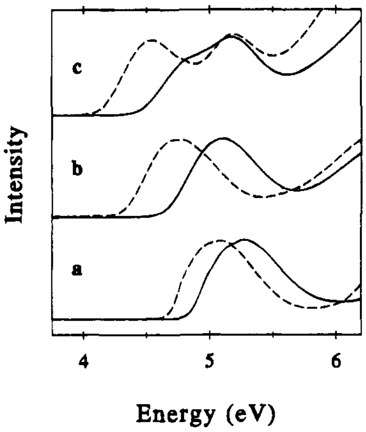


Figure 6. UV–vis absorption spectra of sil(an)yl-substituted thiophene, showing the effect of the increase of the number of silicon atoms in the substituent(s) on the excitation levels in TSi_yMe_{2y+1} (—) and $Me_{2y+1}Si_yTSi_yMe_{2y+1}$ (- - -): (a) $y = 1$; (b) $y = 2$; (c) $y = 4$.

one end (Figure 5). Since the wave function of the intragap exciton level is a modified LUMO, the above description of the stabilizing effect of silicon-containing substituents will be manifest in both exciton and band edge transitions.

One example of the extension of our work on model compounds to include longer silanyl groups is presented in Figure 6. End-capping of thiophene with tetrasilanyl groups leads to increased red shifts when compared with disilanyl caps; additionally, local excitations in the tetrasilanyl parts are observed at 5.19 eV. The extended study of model compounds will be published separately.

Absorption is found to be enhanced by the addition of sil(an)yl groups, two silicon atoms being more effective than one. These trends are most pronounced for thiophene and T_1 derivatives; they are virtually absent for T_6Oct_2. Polymers generally show the highest values for the extinction coefficients. It is unclear why the T_1-based polymer is an exception to this rule.

The difference in absorption energies between oligomer and polymer is found to decrease with increasing length of the oligothiophene block. This is shown in Figure 7, in which both the absorption maxima (Figure 7a) and the E_{0-0} values (Figure 7b) are plotted *vs* the reciprocal of the size, x, of the oligothiophene block (E_{0-0} values were estimated from the intersection of absorption and fluorescence spectra). Our finding is consistent with a spatial confinement of the electronic levels involved to the oligothiophene block proper as it grows in length; i.e., both HOMO and LUMO acquire true π character.[25] Functionally, the oligothiophene blocks become more separated from the oligosilylene blocks and from each other (quantum wells). This is in agreement with the recently reported finding that the effect of silyl substituents on the optical transitions in isothianaphthene oligomers is negligible even for the dimer;[26] the latter has a HOMO–LUMO gap of only 1 eV.

The polymers as well as the oligomers exhibit solvatochromism in solution, similar to poly(3-alkylthiophene)s. Absorption maxima are red shifted 5–10 nm in CH_2Cl_2 with respect to hexane. Spectral shifts are also induced by changing alkyl substituents in the polymers. The replacement of methyl substituents on the silicon atoms by butyl chains results in a small red shift. The introduction of octyl substituents on sexithiophene is found to produce a 20 nm blue shift in spite of the electron-donating character of these substituents, which is obviously due to reduced copolanarity of the rings.[20]

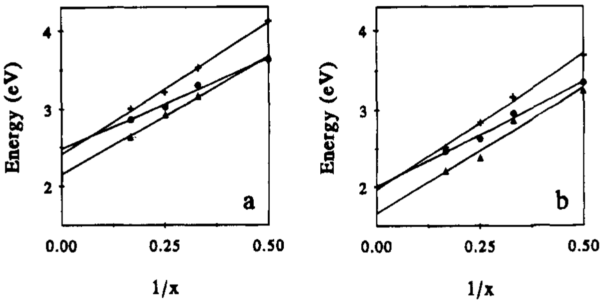


Figure 7. Evolution of the transition energies of thiophene oligomers, T_x, in n-hexane solution (+) and of related polymers, p-$T_xSi_2Bu_4$, in n-hexane solution (●) and thin film (▲) with the reciprocal of the number of rings, x, in the oligothiophene unit ($x = 2$, 3, 4, and 6; in the latter case, the polymer is p-$T_6Oct_2Si_2Bu_4$): (a) energies of absorption maxima; (b) E_{0-0}.

In the solid state, the spectral properties of the polymers are modified. The comparison with solution can only be made for the polymers that have butyl substituents on the silicon atoms, since only these are film-forming. The absorption band of the solid is red-shifted with respect to that of the solution and this shift is increasing for increasing length of the oligothiophene block (Figure 3). We attribute this to the existence of appreciable π-stacking interactions in the solid film of polymers with long oligothiophene blocks. Such a "layering" of aromatic systems will reduce the band gap. Whereas a close packing of planar ring systems seems plausible for longer ring systems, it is much less likely in the polymers with short oligothiophene blocks since it will be very much hindered by the oligosilylene blocks with their bulky butyl substituents. The results for the p-$T_xSi_2Bu_4$ films in Figure 3 are also plotted in Figure 7 *vs* the reciprocal of the size, x, of the oligothiophene block. The absorption maxima (Figure 7a) for the films show a gradually increasing red shift with respect to the solution, but the behavior of the E_{0-0} values (Figure 7b) of the films is definitely more discontinuous in the sense that the values for the T_2- and T_3-based polymers are close to the solution values, while those for T_4- and T_6-based polymers are substantially lower. A very similar result was found for p-T_xSiBu_2 polymers, and we therefore attribute this to the different polymerization schemes chosen for the two classes of polymers, which has resulted in low degrees of polymerization for those with T_4 and T_6 blocks and, consequently, different solid-state packing conditions due to chain end effects.

Fluorescence Spectroscopy. Thiophene itself is nonfluorescent, probably because radiationless transitions to a triplet state compete successfully with fluorescence.[27] (This is probably also related to the relative energy levels of the ^1A and ^1B states,[28] about which there is controversy.[29]) The silyl-substituted T_1 model compounds $Me_3SiTSiMe_3$ and $Me_5Si_2TSi_2Me_5$ were also found to be nonfluorescent. It was therefore surprising to find that the polymer p-TSi_2Bu_4 (**3b**) showed considerable fluorescence; its absorption and fluorescence spectra in hexane solution are shown in Figure 8. It is likely that fluorescence in this case originates from an intramolecular excimer, since the emission band is structureless and the apparent Stokes shift is very large, approximately 1 eV (8250 cm^{-1}). The fluorescence maximum is solvent independent and the spectrum does not display a concentration dependence, both of which

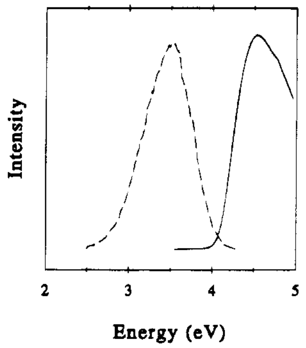


Figure 8. UV–vis absorption (—) and fluorescence (- - -) spectrum of p-TSi_2Bu_4 in *n*-hexane solution. The fluorescence is probably the emission of an intramolecular excimer, since this is the only T_1-based compound that was found to be fluorescent in our present study.

are further indications of the intramolecular nature of the phenomenon.

All compounds having two or more thiophene rings show fluorescence, but the quantum efficiencies show a large variation. While bithiophene shows only a broad band, the fluorescence spectra of the oligothiophenes T_3, T_4, and T_6Oct_2 are characterized by the presence of two distinct peaks and a shoulder (Figure 4). The appearance of multiple peaks has been attributed to the coexistence of distinct conformations (rotamers) of the molecules. They arise because planar conformations are favored by the excitation, and in these, the inter-ring configurations can be either *syn* or *anti* with regard to the position of the sulfur atoms.[30] These details are not discernible in the spectrum of T_2. This may result partly because the signal is weak and noisy, but it is probably mainly determined by the lifetime of the planar excited states. A fluorescence spectrum with features similar to that of the higher oligothiophenes was found for bithiophenes bearing head-to-head (2,2′-) alkyl substituents,[20] which are expected to hinder continuous rotation around the inter-ring bond. In longer oligothiophenes the constraint is probably brought in by the stronger π conjugation.

The very low quantum efficiency of bithiophene in solution, which is at the detection limit of 1%, is raised to 6% by end-capping T_2 with trimethylsilyl groups and further increased to 23% by substitution with pentamethyldisilanyl groups. Longer oligothiophenes have a higher quantum efficiency by themselves, and the silyl end-capping is found to have a much weaker (T_3) or even adverse effect (T_6Oct_2). The polymers based on T_2 blocks have a significantly stronger fluorescence than the corresponding model compounds derived from T_2 and also in these polymers disilanylene blocks give rise to much higher quantum yields than silylene blocks. This strong dependence on the number of silicon atoms is not found for the longer model compounds; in the corresponding polymers the effect is even reversed albeit rather weakly. It must be concluded that the level ordering in T_2 is considerably altered by the substitution, to the effect that excited states become more stable toward the nonradiative processes that compete with fluorescent decay, i.e., internal conversion and intersystem crossing (singlet-to-triplet conversion).[30b,31] Clearly, the stabilization is increasingly less effective, but also less important, for longer oligomers. The trend in the transition energies is the same as that found in absorption: disilanyl(ene) groups provide a red shift with respect to monosilyl(ene) groups.

The effects of a variation of the alkyl substituents are very weak in general. For polymers based on T_2 or longer blocks, the replacement of methyl substituents on silicon by butyl chains results in blue shifts of a few nanometers for the fluorescence maxima, with the exception of p-$T_6Oct_2Si_2Bu_4$. In the dependence of the quantum yields there does not seem to be a clear-cut trend. The introduction of octyl substituents on sexithiophene is found to produce a 5 nm blue shift, which is once more attributed to reduced coplanarity of the rings. The effect is significantly smaller in fluorescence than in absorption since coplanarity is promoted after excitation.[31]

The shift between the absolute maxima of absorption and fluorescence is generally in the range 0.4–0.7 eV (Stokes shift). In organic molecules, part of the shift would correspond to the stabilization of the excited state through a small change in the molecular geometry. In the jargon of conjugated polymers, this is the electron–phonon coupling that gives rise to the exciton state.[10,32] There is no general agreement, however, as to the extent to which the exciton binding energy (the displacement of the exciton levels from the band edges) originates from this effect. Purely electronic interactions, Coulombic and exchange, would produce similar level shifts, but these are said to have a larger impact on the even-parity states that can be reached by two-photon excitations.[10a] It is understood that in the case of charged excitations the extent of the lattice deformation characteristic of a fully relaxed (bi)polaron cannot be realized in a unit as short as bithiophene or even terthiophene, and a longer oligothiophene block is required to accommodate it;[33] the delocalization of a neutral, bound exciton is expected to be more limited.

The composite but ill-resolved nature of the spectra precludes the straightforward determination of a value for the Stokes shift for our compounds. The complexity is even more obvious for the polymer film spectra, which we will now address. For the films the interpretation is further complicated by the apparent presence of additional fluorescence "contaminants". In the case of p-$T_4Si_2Bu_4$ and p-$T_6Oct_2Si_2Bu_4$, the envelope of the film fluorescence resembles that of the solution spectra, whereas in the case of p-$T_2Si_2Bu_4$ and p-$T_3Si_2Bu_4$ the film spectrum is considerably different and broader (Figure 4). This we attribute to the presence of oligothiophene blocks of double length in the polymer chains, i.e., T_4 blocks in p-$T_2Si_2Bu_4$ and T_6 blocks in p-$T_3Si_2Bu_4$, which are a result of undesired coupling reactions. The surplus intensity in the low-energy tail of the two polymer film spectra roughly corresponds to the solution fluorescence of T_4 and T_6, respectively (or rather, of the polymers containing these blocks). Especially in the case of p-$T_3Si_2Bu_4$, the position of the impurity peak agrees well with that of p-$T_6Oct_2Si_2Bu_4$ in solution (which is not strongly shifted from T_6Oct_2). We do not, however, recover the low-energy emission of solid p-$T_6Oct_2Si_2Bu_4$, which in itself suggests that the impurity block is not particularly favorably packed in the matrix. For the other polymers that were prepared *via* the same route (Scheme 2), including those having monosilylene blocks, similar phenomena have been observed.

From the fact that the fluorescence impurities are clearly manifest in the film but do not show up in the solution spectra, we conclude that they fluoresce even when they have not been excited directly; i.e., in the solid they act as an exciton trap. The explanation is

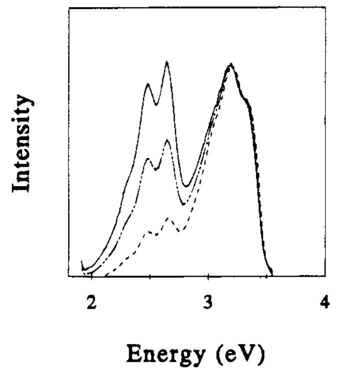


Figure 9. Fluorescence spectra of thin films of a blend of p-T_2SiBu_2 and PMMA, demonstrating fluorescence from excitons trapped in oligothiophene blocks of double length, i.e., T_4 in this case. The films were prepared by spin-coating so as to have an absorption of 0.05 ± 0.01. Compositions p-T_2SiBu_2/PMMA (w/w) tested were 100/0 (—), 50/50 (– – –), and 33/67 (- - -). The curves have been scaled to a common level at the maximum of the fluorescence at 3.10 eV, since an absolute determination of the quantum yield is lacking.

that in the solid, π-stacking as mentioned in the previous section allows further electronic interactions such as the interchain transfer of exciton energy through dipolar effects, or even interchain charge hopping. This makes the trap much more accessible than in solution, where excitons migrate along the chains on which they were created. Furthermore, since a double-length block is expected to have fair quantum efficiency (at least 0.2), the absence of any indication of it in the solution spectra tells us that the concentration of double-length blocks is a few percent at most. Our interpretation implies that the trap fluorescence would be very strongly affected by dilution. This is indeed substantiated by experiments on solid solutions of the polymer p-T_2SiBu_2 in PMMA, the results of which are shown in Figure 9. In this polymer the low-energy peaks are very prominent and their shape closely resembles the solution spectrum of the T_4-based polymer. We observed a strong decrease of these peaks with increasing dilution, which is a strong indication of the trap character of the luminophore.

A general feature of the luminescence spectra is that they are rather broad, even when contaminants are absent. Apart from the phonon dispersion, i.e., the strong coupling of vibrations in the molecular skeleton to the exciton level, there is the inevitable heterogeneous broadening due to conformational disorder in semiflexible polymers. There may be room for improvement here, but the endeavors of creating stereochemically uniform chromophore moieties are constrained by the trade-off between rigidity and processability of the polymer. An alternative route to narrow luminescence spectra may be available by resorting to the above-mentioned mechanism based on the fluorescence of traps that are present in small amounts.

5. Conclusion

We have demonstrated the chemical synthesis of alternating copolymers consisting of well-defined oligothiophene and oligosilylene blocks. Their spectroscopic properties have been explored and were found to show a systematic dependence on the size of the oligothiophene unit. The fluorescence, which is in the visible region, can be adjusted between 400 and 650 nm by a proper choice of the oligothiophene block length. Solution fluorescence efficiencies of the copolymers based on T_2 blocks amounted to 22–58% and thus were very much higher than that of bithiophene itself (1%). We have also demonstrated fluorescence from a polymer based on T_1 blocks, the other blocks being tetrabutyldisilanylene, while thiophene itself and many derivatives of it do not fluoresce. These results are relevant for a possible application of this type of polymer as the active layer in electroluminescent devices. Our present discussion of the properties of solid films has been limited to photoexcitation and photoluminescence, but electroluminescence has been demonstrated and was described in previous papers.[5] Solubility requirements have necessitated the replacement of methyl groups on the silicon atoms by butyls and the introduction of octyl substituents on aromatic blocks longer than quaterthiophene.

From a scientific perspective, the polymers are interesting because of the obvious effects of electronic interaction between the oligothiophene and oligosilylene blocks, a phenomenon commonly referred to as $\pi-\sigma$ conjugation, in a broad sense. This effect is already clearly manifested by end-capped oligothiophenes, and disilanyl substituents are found to have a stronger overlap with the π system than monosilyl groups. The transition energies of polymers are well below those of the corresponding thiophene oligomers (i.e., oligomers that have the same number of rings as the blocks in the polymer) and still lower than those of the end-capped oligomers. The NMR results clearly show that the electronic configuration of the oligothiophene unit differs depending on whether it is part of a polymer or whether it is simply end-capped by silyl groups. With respect to interrupting the conjugation in an extended π system, one silicon atom is at least as effective as two or more. In the polymers, the difference between disilanylene and monosilylene blocks is also significant with respect to fluorescence efficiency, which is much higher in the case of disilanylene blocks. The influence of the oligosilylene blocks on the spectroscopic signature of the oligothiophenes becomes smaller as the number of rings in the latter increases, i.e., as the HOMO–LUMO gap of the oligothiophene block decreases.

The luminescence spectra of poly[(silanylene)thiophene]s are rather broad, which is largely due to conformational disorder. A similar behavior was found in our work on stereochemical tuning,[20] the synthetic aspects of which will be published separately. Our current research is aimed at improving the color purity (reducing the spectral bandwidth) and increasing the quantum yield of the fluorescence. A mechanism that relies on the presence of a small amount of luminescent traps is one possible approach.

6. Experimental Section

6.1. General Procedures. NMR data were recorded at 299.95 (^1H), 75.42 (^{13}C), and 59.59 MHz (^{29}Si) on a Varian (VXR 300) spectrometer operating at 30 °C in the Fourier transform mode. The ^1H NMR chemical shifts are determined relative to the solvent ($CDCl_3$) and converted to the TMS scale using $\delta(CDCl_3) = 7.26$ ppm. The ^{13}C NMR chemical shifts are denoted in δ units (ppm) relative to $\delta(CDCl_3) = 76.91$ ppm. ^{29}Si NMR spectra were recorded using a DEPT pulse sequence. The ^{29}Si NMR chemical shifts are externally referenced to TMS (0 ppm). IR spectra of solids in KBr pellets were recorded on a Mattson Instruments FT-IR spectrometer. Spectra of liquids were taken as neat films on NaCl plates. The absorptions are denoted as s (strong), m (medium), w (weak), br (broad), and sh (shoulder). UV spectra were recorded on a SLM Aminco 3000 ARRAY spectrometer in spectral grade hexane or dichloromethane. Luminescence spectra were recorded on a SLM

Aminco 500. Quantum yields of fluorescence were determined using quinine sulfate (ϕ_F(1 N H_2SO_4) = 0.55) as a standard.[34] Solutions were purged with argon. The GPC results were obtained using a Waters 150-c ALC/GPC system equipped with a PL gel 100 and a TSK gel mixed column at a chloroform flow rate of 1 mL min^{-1}. For calibration polystyrene standards were used. DSC measurements were carried out on a Perkin-Elmer 7 Series thermal analysis system at a heating rate of 20.0 °C/min. Mass spectra were obtained with an AEI MS9 mass spectrometer (Mr. A. Kiewiet, Department of Organic Chemistry, University of Groningen). Elemental analyses were carried out at the Microanalytical Department of the University of Groningen (Mr. J. Ebels and Mr. H. Draaier).

6.2. Materials and Procedures. All reactions were performed under a dry argon atmosphere. Diethyl ether and dimethoxyethane were distilled subsequently from P_2O_5 and $LiAlH_4$. THF was distilled from potassium and $LiAlH_4$. Pentane was distilled from P_2O_5. Thiophene, *n*-BuLi (1.6 or 2.5 M solution in hexane) (Janssen) were used as received. 2,2′-Bithiophene was synthesized according to ref 35. 2,2′:5′,2″-Terthiophene was prepared from 1,4-di-2-thienyl-1,4-butanedione according to ref 36. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA, Janssen) was dried on KOH before use. Dichlorosilanes (Petrarch) were distilled from CaH_2 before use. 1,2-Dichlorotetramethyldisilane and chloropentamethyldisilane were synthesized according to ref 37. 1,4-Dichlorooctamethyltetrasilane was prepared from 1,4-diphenyloctamethyltetrasilane according to ref 38. 1,4-Diphenyloctamethyltetrasilane was prepared from 1-chloro-2-phenyltetramethyldisilane in 90% yield using an excess of sodium in refluxing toluene instead of a sodium–potassium alloy in xylene at 80 °C. 1,2-Dichlorotetra-*n*-butyldisilane was synthesized according to ref 39. Synthesis of the monomers **8a–c** was described in ref 6. Synthesis of 5,5‴-dibromo-3,3‴-di-*n*-octylquaterthiophene was described in ref 19. The catalyst dichloro[1,3-bis(diphenylphosphino)propane]nickel(II) ($NiCl_2$-dppp) was synthesized according to ref 40. Tetrakis(triphenylphosphine)palladium(0) was prepared according to ref 41.

6.3. Monomers. 2,5-Bis(dimethylchlorosilyl)thiophene (2a). TMEDA (10.5 mL, 70 mmol) was added in 10 min to *n*-BuLi (70 mmol, 2.5 M). The mixture was stirred for 15 min without cooling. After dilution with 50 mL of pentane, thiophene (5.9 g, 70 mmol) was added in 15 min at 0 °C. Another 70 mmol of *n*-BuLi was added at 0 °C and stirring was continued. After 30 min, the white suspension formed was slowly added through a wide siphon to dimethyldichlorosilane (420 mmol) in 25 mL of pentane at −40 to −20 °C. The mixture was stirred overnight at ambient temperature. The solution was decanted from the LiCl salt, which was washed with another 50 mL of pentane. The combined organic layers were Kugelrohr distilled (bp 120 °C, 1 mbar), yielding 12.6 g (67%) of **2a** as a colorless viscous liquid. ^1H NMR δ 0.76 (s, 12H), 7.52 (s, 2H) ppm. ^{13}C NMR δ 3.3 (CH_3), 136.7 (CH), 143.3 (C) ppm. ^{29}Si NMR δ 14.8.

2,5-Bis(dibutylchlorosilyl)thiophene (2b) was prepared similar to **2a** from dibutyldichlorosilane and thiophene; yield 74% after Kugelrohr distillation. ^1H NMR δ 0.91 (t, 6H), 1.11 (t, 4H), 1.35–1.49 (m, 8H), 7.50 (s, 2H) ppm. ^{13}C NMR δ 13.5 (CH_3), 17.3 ($SiCH_2$), 24.9, 25.9 (CH_2), 136.8 (CH), 141.5 (C) ppm. ^{29}Si NMR δ 16.8.

1-Chloro-4-(2-thienyl)-1,1,2,2,3,3,4,4-octamethyltetrasilane (9a). An *n*-BuLi·TMEDA–thiophene (20 mmol) solution (as prepared for **2a**) was added to 1,4-dichlorooctamethyltetrasilane (20 mmol) at −20 °C. The mixture was stirred overnight at room temperature. After decanting, the crude concentrated residue was Kugelrohr distilled. ^1H NMR showed the presence of compounds **9a** (80%) and **8c**[6] (20%). This mixture was used for the synthesis of **8d**.

NMR data of **9a**: ^1H NMR δ 0.24 (s, 4H), 0.31 (s, 4H), 0.49 (s, 4H), 0.58 (s, 4H), 7.22 (d, 1H), 7.24 (d, 1H), 7.64 (dd, 1H) ppm. ^{13}C NMR δ −6.3, −5.9, −1.6, 3.2 ($SiCH_2$), 128.2, 130.4, 134.0, (CH), 138.5 (C) ppm.

Dibutylchloro(2-thienyl)silane (9b). An *n*-BuLi·TMEDA–thiophene (0.14 mol) solution in diethyl ether (75 mL) was added to dibutyldichlorosilane (30 g, 0.14 mol) at −20 °C while the temperature was kept between 0 and 10 °C during addition. Stirring was continued at room temperature overnight. After addition of pentane (200 mL) to the reaction mixture, the lithium salts could be filtered off under dry Ar. After removal of the solvent in vacuo, the residue was Kugelrohr distilled (100 °C/0.1 mbar) to provide 30.7 g (84%) of spectroscopically pure product, which was used without further purification. ^1H NMR δ 0.92 (t, 6H, CH_3), 1.11 (t, 4H, $SiCH_2$), 1.44 (m, 8H, CH_2), 7.24 (dd, 1H, C(3)-H), 7.44 (d, 1H, C(4)-H), 7.69 (d, 1H, C(5)-H) ppm. ^{13}C NMR δ 13.5 (CH_3), 17.2 ($SiCH_2$), 25.0, 25.9, 128.2, 132.0, 135.9 (CH), 134.0 (C) ppm.

1,8-Bis(2-thienyl)hexadecamethyloctasilane (8d). A mixture of **8c** and **9a** (6.1 g, 20 mmol) was added slowly to a sodium dispersion (1.38 g, 60 mmol) in refluxing toluene. After complete addition, refluxing was continued for 2 h. After cooling to room temperature, excess sodium and sodium chloride were removed by filtration. After evaporation of the solvent, column purification (Kieselgel-60, pentane) provided 1.8 g (28%) of **8d** as a white solid, mp 106–107 °C. ^1H NMR[42] δ 0.121, 0.126, 0.132, 0.163, 0.169, 0.170, 0.176, 0.181, 0.197, 0.203, 0.210, 0.214, 0.431, 0.435 (all CH_3), 7.20 (d, 2H), 7.59 (dd, 1H) ppm. ^{13}C NMR δ −5.5, −4.5, −4.4, −4.2, −4.1, −4.06, −4.03, −1.6 (CH_3), 128.1, 130.2, 133.9 (CH), 139.2 (C) ppm. ^{29}Si NMR δ −43.1, −39.0, −38.9, −37.7, −37.6, −37.53, −37.48, −20.1 ppm. IR 2949 (s), 2892 (m), 2787 (w), 1401 (m), 1320 (s), 1247 (s), 1209 (m), 983 (m), 829 (s), 756 (s). MS *m/e* (rel intensity) 630 (M^+, 7), 615 ($M^+ - CH_3$, 1), 315 ($M^+/2$, 100). Exact mass determination calcd for $C_{24}H_{54}S_2Si_8$: 630.181. Found: 630.182.

Bis(2-thienyl)dibutylsilane (8e). TMEDA (16.24 g, 0.14 mol) was added to a stirred solution of *n*-BuLi (0.14 mol). Thiophene (11.84 g, 0.14 mol) in 50 mL of pentane was slowly added to the BuLi·TMEDA solution at −20 °C. The temperature was kept between 0 and 10 °C. After addition of ether (85 mL), the reaction mixture was stirred for 30 min. This BuLi·TMEDA–thiophene solution was added with a syringe to dibutyldichlorosilane (15 g, 0.07 mol) at −20 °C. The temperature was slowly raised to room temperature and stirring was continued overnight. The reaction mixture was poured in 300 mL of a 5% aqueous solution of NH_4Cl and extracted with ether. The ether layers were washed with brine and dried on Na_2SO_4. The solvent was removed by distillation, and the residue was Kugelrohr distilled (140 °C/0.1 mbar) to provide 16.4 g (76%) of **8e**.

^1H NMR δ 1.03 (t, 6H, CH_3), 1.26 (t, 4H, $SiCH_2$), 1.54 (m, 8H, CH_2), 7.32 (dd, 2H, C(3)-H), 7.48 (dd, 2H, C(4)-H), 7.73 (dd, 2H, C(5)-H) ppm. ^{13}C NMR δ 13.6 (CH_3), 14.5 ($SiCH_2$), 25.8, 26.4 (CH_2), 128.0, 131.2, 135.8 (CH), 135.4 (C) ppm. UV λ_{max} = 238 nm, ϵ = 18000. IR 3073 (w), 2958 (s), 2925 (s), 2858 (m), 1464 (m), 1405 (m), 1214 (m), 1084 (m), 992 (m), 852 (m), 748 (m). Anal. Calcd for $C_{16}H_{24}S_2Si$: C, 62.28; H, 7.84; S, 20.78. Found: C, 62.66; H, 8.17; S, 19.65. MS *m/e* (rel intensity) 308 (M^+, 13), 251 ($M^+ - C_4H_9$, 40). Exact mass determination Calcd for $C_{16}H_{42}SiS_2$: 308.109. Found: 308.109.

1,2-Bis(2-thienyl)-1,1,2,2-tetrabutyldisilane (8f). Dibutylchloro(2-thienyl)silane (29.5 g, 0.11 mol) was slowly added to vigorously stirred sodium sand (7.8 g, 0.34 mol) in 100 mL of refluxing toluene. The solution was refluxed for another 2 h. After filtration and washing of the sodium salts with toluene, the solvent was removed by rotary evaporation and the crude product was Kugelrohr distilled (220 °C/1 mbar). The residue was purified by flash chromatography (Kieselgel-60/pentane), yielding 15.2 g (60%) of the title product as a colorless oil. ^1H NMR δ 0.95 (t, 12H, CH_3), 1.05 (t, 8H, $SiCH_2$), 1.43 (m, 16H, CH_2), 7.23 (d, 2H, C(3)-H), 7.24 (s, 2H, C(4)-H), 7.64 (dd, 2H, C(5)-H) ppm. ^{13}C NMR δ 13.4 ($SiCH_2$), 13.7 (CH_3), 26.7 (CH_2), 128.0, 130.5, 134.9 (CH), 136.3 (C) ppm. UV λ_{max} = 247 nm, ϵ = 19600. IR 3075 (w), 2957 (s), 2924 (s), 2858 (m), 1463 (m), 1406 (m), 1213 (m), 1082 (m), 981 (m), 849 (m), 747 (m). Anal. Calcd for $C_{24}H_{42}Si_2S_2$: C, 63.93; H, 9.39; S, 14.22. Found: C, 63.97; H, 9.38; S, 14.26. MS *m/e* (rel intensity) 450 (M^+, 31), 393 ($M^+ - C_4H_9$, 43), 337 ($M^+ - C_8H_{17}$, 37), 225 ($M^+/2$, 26), 169 ($M^+/2 - C_4H_8$, 69), 113 ($M^+/2 - C_8H_{16}$, 92), 111 ($M^+/2 - C_8H_{18}$, 20), 85 ($M^+/2 - SiC_8H_{16}$, 28). Exact mass determination calcd for $C_{24}H_{42}S_2Si_2$: 450.226. Found: 450.227.

5,5′-Dibromo-2,2′-bithienyl (10). 2,2′-Bithiophene (26 g, 155 mmol) was dissolved in 250 mL of dry chloroform. After addition of acetic acid (250 mL), 2 equiv of NBS (55 g, 310 mmol) was added over a period of 1−2 h in portions of 1−4 g. After refluxing for 0.5 h, the reaction mixture was cooled and poured into 500 mL of CS_2. The mixture was washed with portions of 150 mL of a KOH solution (0.18 N), until a basic solution was obtained and subsequently washed with water and brine and dried over $MgSO_4$. After removal of the solvent, the crude product was crystallized from chloroform to give 35.8 g (83%) of the title product. ^{1}H NMR δ 6.85 (d, 2H, CH), 6.96 (d, 2H, CH) ppm. ^{13}C NMR δ 111.5 (CBr), 124.1/130.6 (CH), 137.8 (C) ppm.

6.4. Polymers. Poly[2,5-(tetramethyldisilanylene)thiophene] (3a; p-TSi$_2$Me$_4$). A solution of 4.03 g of **2a** in 10 mL of toluene was added dropwise to 0.87 g of sodium in refluxing toluene. The mixture immediately turned purple/black. After stirring for 2 h, the reaction mixture was cooled to room temperature and poured into 1 L of 2-propanol containing sodium bicarbonate (10 g). The white precipitate was filtered, dried, dissolved in methylene chloride, and purified by precipitation in ethanol, affording 1.46 g (47%) of polymer **3a**.

^{1}H NMR δ 0.39 (s, 12H, CH_3), 7.2 (s, 2H, CH) ppm. ^{13}C NMR δ −2.6 (CH_3), 135.6 (CH), 143.9 (C) ppm. ^{29}Si NMR δ −24.8 ppm. UV λ_{max} = 270 nm. IR 2953 (m), 1484 (w), 1280 (m), 1246 (s), 1200 (m), 1006 (s), 831 (s), 786 (s). Anal. Calcd $C_8H_{14}SSi_2$: C, 48.42; H, 7.11; S, 16.16. Found: C, 48.35; H, 7.25; S, 15.17.

Poly[2,5-(tetrabutyldisilanylene)thiophene] (3b; p-TSi$_2$Bu$_4$). Wurtz-type coupling of **3b** was performed similar to **3a** from 4.37 g (10 mmol) of **5** and 0.51 g of sodium, affording 0.45 g (12%) of polymer **3b**. ^{1}H NMR δ 0.85 (t, 12H, CH_3), 0.91 (t, 8H, $SiCH_2$), 1.35 (m, 16H, CH_2), 7.18 (bs, 2H) ppm. ^{13}C NMR δ 13.4 ($SiCH_2$), 13.6 (CH_3), 26.7, 26.8 (CH_2), 135.8 (CH), 142.2 (C) ppm. ^{29}Si NMR −21.7 ppm. UV λ_{max} = 274 nm, ϵ = 9400 (per unit).

Poly[5,5′-(dimethylsilylene)-2,2′-bithiophene] (6a; p-T$_2$SiMe$_2$). To a solution of 2,2′-bithiophene (1.66 g, 10 mmol) in 35 mL of dimethoxyethane, *n*-BuLi (10.2 mmol) was added dropwise at −60 °C. After stirring for 15 min, another 10.2 mmol of *n*-BuLi was added. The temperature was raised to room temperature within 30 min, during which the white lithium salt started to precipitate from the reaction mixture. After stirring for 2 h, the reaction mixture was cooled to −20 °C and a solution of dichlorodimethylsilane (1.29 g, 10 mmol) in 15 mL of dimethoxyethane was added slowly without further cooling. The temperature was raised to room temperature within 2 h and stirring was continued overnight. The reaction mixture was poured into a cold mixture of 40 mL of 5% aqueous NH_4Cl and 200 mL of methanol. The precipitate was collected after stirring for 30 min, washed with methanol, water, and ether, and vacuum dried at 40 °C. The crude product was dissolved in thiophene and precipitated in respectively methanol and acetone, yielding 1.0 g (45%) of polymer. ^{1}H NMR δ 0.64 (s, 6H, CH_3), 7.21 (d, 2H, CH), 7.25 (d, 2H, CH) ppm. ^{13}C NMR δ −0.3 (CH_3), 125.5/136.2 (CH), 137.0/143.4 (C) ppm. ^{29}Si NMR δ −15.3 ppm. UV λ_{max} = 326 nm. IR 3065 (w), 2956 (w), 1492 (w), 1421 (m), 1251 (m), 1196 (m), 1074 (m), 991 (s), 874 (m), 832 (m), 798 (s). Anal. Calcd for $C_{10}H_{10}S_2Si$: C, 54.01; H, 4.53; S, 28.83. Found: C, 53.97; H, 4.58; S, 28.38.

Poly[5,5′-(tetramethyldisilanylene)-2,2′-bithiophene] (6b; p-T$_2$Si$_2$Me$_4$). The same procedure as for **6a** was followed using dichlorotetramethyldisilane (1.87 g, 10 mmol) in 15 mL of DME. The same workup procedure yielded 60% of polymer. GPC and NMR showed that the polymer contained approximately 5% cyclic material. ^{1}H NMR δ 0.42 (s, 12H, CH_3), 7.05 (d, 2H, CH), 7.22 (d, 2H, CH) ppm. ^{13}C NMR δ −2.9 (CH_3), 125.3/135.3 (CH), 137.4/142.8 (C) ppm. ^{29}Si NMR δ −24.5 ppm. UV λ_{max} = 331 nm. IR 3067 (w), 2951 (m), 2892 (w), 1419 (m), 1240 (m), 1193 (m), 1070 (m), 984 (s), 872 (m), 830 (m), 789 (s). Anal. Calcd for $C_{12}H_{16}S_2Si_2$: C, 51.37; H, 5.75; S, 22.86. Found: C, 51.24; H, 5.82; S, 21.69.

Poly[5,5″-(dimethylsilylene)-2,2′:5′,2″-terthiophene] (7a; p-T$_3$SiMe$_2$). The same procedure was followed with 2,2′:5′,2″-terthiophene (1.24 g, 5 mmol) in 25 mL of dimethoxyethane. Dichlorodimethylsilane (0.65 g, 5 mmol) in 10 mL of dimethoxyethane was added to the dilithio derivative of **5**. After the usual workup, 60% of polymer **7a** was isolated. ^{1}H NMR δ 0.66 (s, 6H, CH_3), 7.09 (s, 2H, CH), 7.23 (d, 2H, CH), 7.23 (d, 2H, CH) ppm. ^{13}C NMR δ −0.3 (CH_3), 124.7, 125.1, 136.3 (CH), 136.7, 136.8, 143.3 (C) ppm. ^{29}Si NMR δ −15.2 ppm. UV λ_{max} = 370 nm. IR 3054 (w), 2951 (w), 1493 (w), 1427 (s), 1251 (s), 1197 (m), 1070 (s), 990 (s), 831 (m), 793 (s). Anal. Calcd for $C_{14}H_{12}S_3Si$: C, 55.22; H, 3.97; S, 31.59. Found: C, 55.06; H, 3.98; S, 30.78.

Poly[5,5″-(tetramethyldisilanylene)terthiophene] (7b; p-T$_3$Si$_2$Me$_4$). The same procedure was followed using 2,2′:5′,2″-terthiophene (1.24 g, 5 mmol) in 25 mL of dimethoxyethane. Dichlorotetramethyldisilane (0.94 g, 5 mmol) in 10 mL of dimethoxyethane was added. The isolated polymer (40%) contained small amounts of cyclic material. ^{1}H NMR δ 0.42 (s, 12H, CH_3), 7.05 (d, 2H, CH), 7.07 (s, 2H, CH), 7.21 (d, 2H, CH) ppm. ^{13}C NMR δ −3.0 (CH_3), 124.4, 125.0, 135.3 (CH), 136.2, 137.6, 142.5 (C) ppm. ^{29}Si NMR δ −24.4 ppm. UV λ_{max} = 369 nm. IR 3056 (w), 2950 (m), 2891 (w), 1425 (m), 1246 (m), 1194 (m), 1068 (m), 982 (s), 829 (m), 786 (s). Anal. Calcd for $C_{16}H_{18}S_3Si_2$: C, 52.99; H, 5.00; S, 26.52. Found: C, 51.05; H, 4.96; S, 25.57.

Poly[5,5′-(dibutylsilylene)-2,2′-bithiophene] (6c; p-T$_2$SiBu$_2$). The same procedures were followed as for the polymers with methyl substituents. The dichlorodisilanes were added at −40 °C and after stirring overnight, the reaction mixture was refluxed for 1 h. Precipitation from chloroform in methanol and acetone, respectively, gave the polymers in yields of 40−55%. The reactions with disilanes gave approximately 5−10% cyclic product, which could be isolated from the acetone fraction and purified by crystallization. ^{1}H NMR δ 0.89 (t, 6H, CH_3), 1.09 (q, 4H, $SiCH_2$), 1.4 (m, 8H, CH_2), 7.21 (d, 2H,CH), 7.28 (d, 2H, CH) ppm. ^{13}C NMR δ 13.7 (CH_3), 14.4 ($SiCH_2$), 25.8, 26.5 (CH_2), 125.3, 136.9 (CH), 135.0, 143.2 (C) ppm. ^{29}Si NMR δ −13.0 ppm. UV λ_{max} = 330 nm, ϵ = 12900. IR (film on KBr pellet) 3061 (w), 2957 (s), 2923 (s), 2871 (m), 1463 (m), 1420 (m), 1263 (w), 1197 (m), 1079 (m), 990 (s), 905 (m), 874 (m), 797 (s). Anal. Calcd for $C_{16}H_{22}S_2Si$: C, 62.69; H, 7.23; S, 20.92. Found: C, 62.58; H, 7.17; S, 20.70.

Poly[5,5′-(tetrabutyldisilanylene)-2,2′-bithiophene] (6d; p-T$_2$Si$_2$Bu$_4$). ^{1}H NMR δ 0.87 (t, 12H, CH_3), 0.96 (q, 8H, $SiCH_2$), 1.34 (m, 16H, CH_2), 7.03 (d, 2H, CH), 7.25 (d, 2H, CH) ppm. ^{13}C NMR δ 13.3 (CH_3), 13.6 ($SiCH_2$), 26.7 (CH_2), 125.1, 135.9 (CH), 136.0, 142.6 (C) ppm. ^{29}Si NMR δ −21.1 ppm. UV λ_{max} = 342 nm, ϵ = 21200. IR (film on KBr pellet) 3058 (w), 2956 (s), 2923 (s), 2871 (m), 1635 (w), 1462 (m), 1417 (m), 1196 (m), 1078 (m), 980 (m), 872 (m), 795 (s). Anal. Calcd for $C_{24}H_{40}S_2Si_2$: C, 64.22; H, 8.98; S, 14.29. Found: C, 64.70; H, 9.09; S, 13.79.

Poly[5,5″-(dibutylsilylene)terthiophene] (7c; p-T$_3$SiBu$_2$). ^{1}H NMR δ 0.91 (t, 6H, CH_3), 1.11 (q, 4H, $SiCH_2$), 1.43 (m, 8H, CH_2), 7.11 (s, 2H, CH), 7.23 (d, 2H, CH), 7.26 (d, 2H, CH) ppm. ^{13}C NMR δ 13.7 (CH_3), 14.4 ($SiCH_2$), 25.8/26.4 (CH_2), 124.7, 124.9, 136.9 (CH), 134.9, 136.2, 143.2 (C) ppm. ^{29}Si NMR δ −13.1 ppm. UV λ_{max} = 379 nm, ϵ = 31900. IR (film on KBr pellet) 3060 (w), 2956 (s), 2923 (s), 2870 (m), 1460 (m), 1427 (m), 1196 (m), 1079 (m), 988 (m), 871 (m), 792 (s). Anal. Calcd for $C_{20}H_{24}S_3Si$: C, 61.80; H, 6.22; S, 24.75. Found: C, 61.50; H, 6.31; S, 24.02.

Poly[5,5″-(tetrabutyldisilanylene)terthiophene] (7d; p-T$_3$Si$_2$Bu$_4$). ^{1}H NMR δ 0.88 (t, 12H, CH_3), 0.97 (q, 8H, $SiCH_2$), 1.35 (m, 16H, CH_2), 7.04 (d, 2H, CH), 7.08 (s, 2H, CH), 7.22 (d, 2H, CH) ppm. ^{13}C NMR δ 13.3 (CH_3), 13.6 ($SiCH_2$), 26.7 (CH_2), 124.3, 124.9, 135.9 (CH), 136.2, 136.3, 142.4 (C) ppm. ^{29}Si NMR δ −21.1 ppm. UV λ_{max} = 378 nm, ϵ = 32200. IR (film on KBr pellet) 3067 (w), 2956 (s), 2923 (s), 2856 (m), 1636 (w), 1458 (m), 1426 (m), 1195 (m), 1079 (m), 979 (m), 870 (m), 792 (s). Anal. Calcd for $C_{28}H_{42}S_3Si_2$: C, 63.33; H, 7.97; S, 18.11. Found: C, 62.63; H, 7.62; S, 18.16.

Poly[(dibutylsilylene)quaterthiophene] (11a; p-T$_4$SiBu$_2$). Bis(2-thienyl)dibutylsilane (1.54 g, 5 mmol) was dissolved in 25 mL of THF, and 5 mmol of *n*-BuLi was added at −40 °C. After stirring for 15 min, another 5 mmol of *n*-BuLi was added and the solution was stirred for 2 h. $ZnCl_2$ (1.36 g, 10 mmol) was added at −20 °C and stirring was continued for 1 h at 0 °C. After addition of $Pd(PPh_3)_4$ (150 mg, 0.15 mmol), 5,5′-dibromobithienyl (1.63 g, 5 mmol) in 25 mL of THF was added. The temperature was raised at 45 °C for 2 h (the reaction mixture slowly became red) and the reaction mixture was refluxed overnight. The reaction mixture was poured into 200 mL of a methanol−NH_4Cl (10 g) mixture and stirred for 60 min. The solid material was dissolved in chloroform and precipitated in cold acetone. After stirring for 1 h, the acetone was decanted. The polymer was washed with acetone and vacuum dried, yielding 860 mg (40%) of pure product. The fraction soluble in acetone was precipitated in cold methanol and after filtration vacuum dried as well, yielding 600 mg (28%) of polymer **11a**. ^1H NMR δ 0.93 (t, 6H, CH_3), 1.14 (m, 4H, $SiCH_2$), 1.44 (m, 8H, CH_2), 7.07 (s, 2H, CH), 7.12 (s, 2H, CH), 7.25 (s, 2H, CH), 7.27 (s, 2H, CH) ppm. ^{13}C NMR δ 13.7 (CH_3), 14.3 ($SiCH_2$), 25.6/26.5 (CH_2), 124.4, 124.7, 125.0, 136.7 (CH), 134.9, 136.0, 136.1, 143.1 (C) ppm. UV λ_{max} = 418 nm, ϵ = 18600. IR (film on KBr pellet) 3060 (w), 2953 (m), 2919 (m), 2867 (m), 1491 (m), 1424 (m), 1194 (m), 1072 (m), 986 (s), 789 (s). Anal. Calcd for $C_{24}H_{26}S_4Si$: C, 58.40; H, 5.18; S, 26.57; Br, 4.41. Found: C, 58.51; H, 5.46; S, 24.69; Br, 3.21.

Poly[(tetrabutyldisilanylene)quaterthiophene] (11b; p-$T_4Si_2Bu_4$). The same procedure as for **11a** was followed. 5,5′-Dibromobithienyl in 20 mL of THF was added to the $ZnCl_2$ derivative of 1,2-bis(2-thienyl)-1,1,2,2-tetrabutyldisilane (1.8 g, 4 mmol) in 20 mL of THF, yielding 0.78 g (32%) of polymer. ^1H NMR δ 0.92 (t, 12H, CH_3), 1.01 (m, 8H, $SiCH_2$), 1.39 (m, 16H, CH_2), 7.08 (s, 2H, CH), 7.10 (s, 2H, CH), 7.23 (s, 2H, CH), 7.25 (s, 2H, CH) ppm. ^{13}C NMR δ 13.2 ($SiCH_2$), 13.7 (CH_3), 26.7 (CH_2), 124.2, 124.4, 125.0, 135.9 (CH), 135.6, 136.3, 136.4, 142.2 (C) ppm. UV λ_{max} = 417 nm, ϵ = 33200. IR (film on KBr pellet) 3065 (w), 2956 (s), 2923 (s), 2870 (m), 1461 (m), 1195 (m), 1080 (m), 978 (m), 871 (m), 790 (s). Anal. Calcd for $C_{32}H_{44}S_4Si_2$: C, 60.37; H, 6.81; S, 20.84; Br, 3.46. Found: C, 60.09; H, 6.93; S, 20.53; Br, 2.57.

Poly[(dibutylsilanylene)-4′,3′′′′′-di-*n*-octylsexithiophene] (13e; p-$T_6Oct_2SiBu_2$). To a solution of bis(2-thienyl)dibutylsilane (1.08 g, 3.5 mmol) in 30 mL of dimethoxyethane, *n*-BuLi (1.5 mL, first equiv) was added dropwise at −60 °C. After stirring for 15 min, the temperature was raised to −20 °C. Another 1.5 mL of *n*-BuLi (second equiv) was added, again at −60 °C. The solution was stirred for 1.5 h while the temperature slowly rose to 10 °C. Separately, $MgBr_2 \cdot OEt_2$ was prepared using the following procedure. 1,2-Dibromoethane (1.41 g, 7.5 mmol) was slowly added to magnesium turnings (0.37 g, 7.5 mmol) in 6 mL of diethyl ether. After refluxing for 30 min, this reagent was added to the dilithium salts of bis(2-thienyl)dibutylsilane at −20 °C. The temperature was raised to room temperature and 50 mg of $NiCl_2 \cdot dppp$ was added. To the reaction mixture the 5,5′′′-dibromo-3,3′′′-di-*n*-octylquaterthiophene (2.5 g, 3.5 mmol) in 20 mL of dimethoxyethane was added in 10−20 min. The temperature rose to 30−35 °C (the reaction mixture slowly became red-brownish) and stirring was continued overnight. After addition of another 100 mg of $NiCl_2 \cdot dppp$, the solution was refluxed for 2 h, concentrated, and poured into a cold 5% aqueous mixture of NH_4Cl and methanol. The sticky gum was collected and vacuum dried, dissolved in CH_2Cl_2, filtered, and precipitated in cold acetone. The acetone solution was decanted and the sticky material vacuum dried, yielding 1.6 g (53%) of **13e**. ^1H NMR δ 0.92 (s, 12H, CH_3(Oct+Bu)), 1.13 (s, 4H, $SiCH_2$), 1.32 (s, 20H, CH_2(Oct)), 1.43 (s, 8H, CH_2(Bu)), 1.69 (s, 4H, β-CH_2 (Oct)), 2.79 (s, 4H, α-CH_2), 7.07 (bs, 4H, CH), 7.15 (bs, 2H, CH), 7.27 (bs, 4H, CH) ppm. ^{13}C NMR δ 13.7 (CH_3/Bu), 14.1 (CH_3/Oct), 14.4 ($SiCH_2$/Bu), 22.7 (α-CH_2/Oct), 25.8, 26.5 (CH_2/Bu), 29.3, 29.4, 29.5, 29.9, 30.5, 31.9 (CH_2/Oct), 123.9, 124.9, 126.3, 127.1, 136.9 (CH), 129.6, 134.8, 135.0, 135.2, 136.7, 140.5, 143.1 (C) ppm. UV λ_{max} = 430 nm, ϵ = 40700. IR (film on KBr pellet) 3064 (w), 2955 (m), 2952 (s), 2854 (m), 1462 (m), 1217 (m), 1073 (m), 989 (m), 715 (s). Anal. Calcd for $C_{48}H_{62}S_6Si$: C, 65.21; H, 7.04; S, 21.76; Br, 3.19. Found: C, 64.33; H, 7.31; S, 20.82; Br, 2.99.

Poly[(tetrabutyldisilanylene)-4′,3′′′′′-di-*n*-octylsexithiophene] (13f; p-$T_6Oct_2Si_2Bu_4$). The same procedure was followed as for polymer **13e**, yielding 1.9 g (54%) of polymer. ^1H NMR δ 0.89 (s, 18H, CH_3(Oct+Bu)), 0.96 (s, 8H, $SiCH_2$), 1.30 (s, 20H, CH_2(Oct)), 1.35 (s, 16H, CH_2(Bu)), 1.68 (s, 4H, β-CH_2(Oct)), 2.77 (s, 4H, α-CH_2), 7.03 (bs, 4H, CH), 7.13 (bs, 2H, CH), 7.21 (bs, 4H, CH) ppm. ^{13}C NMR δ 13.1 ($SiCH_2$/Bu), 13.7 (CH_3/Bu), 14.1 (CH_3/Oct), 22.7 (α-CH_2/Oct), 26.7 (CH_2/Bu), 29.3, 29.4, 29.6, 30.5, 39.2 (CH_2/Oct), 123.9, 125.0, 126.3, 126.7, 135.9 (CH), 129.5, 134.9, 135.1, 135.3, 136.7, 140.6, 142.3 (C) ppm. UV λ_{max} = 441 nm, ϵ = 39300. IR (film on KBr pellet) 3064 (w), 2958 (m), 2924 (s), 2855 (m), 1459 (m), 1376 (w), 1192 (m), 1079 (m), 979 (m), 793 (m). Anal. Calcd for $C_{56}H_{80}S_6Si_2$: C, 65.74; H, 7.80; S, 19.08; Br, 2.38. Found: C, 65.32; H, 7.91, S, 18.77; Br, 2.02.

Poly[(dimethylsilanylene)-4′,3′′′′′-di-*n*-octylsexithiophene] (13a; p-$T_6Oct_2SiMe_2$). The reaction was performed as for polymer **13e** using bis(2-thienyl)dimethylsilane (0.78 g, 3.5 mmol) in THF and gave 2.17 g (80%) of **13a** as a red solid. ^1H NMR δ 0.68 (s, 6H, $SiCH_3$), 0.89 (s, 6H, CH_3), 1.30 (m, 20H, CH_2), 1.69 (s, 4H, β-CH_2), 2.77 (m, 4H, α-CH_2), 7.02 (m, 4H), 7.06 (d, 2H), 7.12 (d, 2H), 7.21 (d, 2H) ppm. ^{13}C NMR δ 0.3 ($SiCH_3$), 14.1 (CH_3), 22.7 (α-CH_2/Oct), 29.3, 29.4, 29.5, 30.4, 31.9 (CH_2), 123.9, 125.0, 126.3, 127.1, 136.3 (CH), 129.7, 134.9, 135.0, 136.7, 140.5, 143.2 (C) ppm. UV λ_{max} = 415 nm, ϵ = 45400. Anal. Calcd for $C_{42}H_{50}S_6Si$: C, 65.06; H, 6.50; S, 24.81. Found: C, 64.47; H, 6.48; S, 24.52.

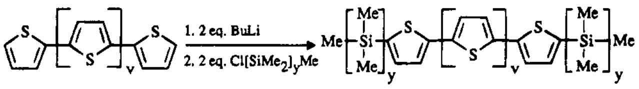
Poly[(tetramethyldisilanylene)-4′,3′′′′′-di-*n*-octylsexithiophene] (13b; p-$T_6Oct_2Si_2Me_4$). The reaction was performed as for polymer **13e** using bis(2-thienyl)tetramethyldisilanylene (1.41 g, 5 mmol) in THF and gave 3.46 g (83%) of **13b** as a red solid. ^1H NMR δ 0.46 (s, 12H, $SiCH_3$), 0.90 (s, 6H, CH_3), 1.30 (m, 20H, CH_2), 1.67 (m, 4H, β-CH_2), 2.77 (m, 4H, α-CH_2), 7.02 (m, 4H), 7.06 (d, 2H), 7.12 (d, 2H), 7.21 (d, 2H) ppm. ^{13}C NMR δ −2.9 ($SiCH_3$), 14.0 (CH_3), 22.6 (α-CH_2/Oct), 29.2, 29.3, 29.4, 30.4, 31.8 (CH_2), 123.8, 124.9, 126.2, 126.6, 135.3 (CH), 129.3, 135.0, 135.4, 136.7, 139.4, 140.5, 142.0 (C) ppm. ^{29}Si NMR δ −24.4 ppm. UV λ_{max} = 423 nm, ϵ = 44300. IR (film on KBr pellet) 2953 (m), 2925 (s), 2854 (m), 1631 (m), 1458 (s), 1247 (s), 1068 (s), 984 (m), 829 (m), 788 (s).

Poly[(octamethyltetrasilanylene)-4′,3′′′′′-di-*n*-octylsexithiophene] (13c; p-$T_6Oct_2Si_4Me_8$). The reaction was performed as for polymer **13e** using 1,4-bis(2-thienyl)octamethyltetrasilanylene (1.99 g, 5 mmol) in THF and gave 3.7 g (78%) of **13c** as a red solid. ^1H NMR δ 0.15 (s, 12H, $SiCH_3$), 0.42 (s, 12H, $SiCH_3$), 0.90 (bs, 6H, CH_3), 1.30 (m, 20H, CH_2), 1.67 (m, 4H, β-CH_2), 2.77 (m, 4H, α-CH_2), 7.02 (m, 4H), 7.06 (d, 2H), 7.12 (d, 2H), 7.21 (d, 2H) ppm. ^{13}C NMR δ −5.8, −1.8 ($SiCH_3$), 14.0 (CH_3), 22.6 (α-CH_2/Oct), 29.2, 29.3, 29.4, 30.4, 31.8 (CH_2), 123.8, 124.9, 126.2, 126.6, 134.8 (CH), 129.1, 135.1, 135.4, 136.7, 139.4, 140.5, 142.0 (C) ppm. ^{29}Si NMR δ −44.4, −20.1 ppm. UV λ_{max} = 424 nm, ϵ = 38500. IR (film on KBr pellet) 2952 (s), 2926 (s), 2854 (m), 1499 (m), 1462 (s), 1246 (m), 1068 (w), 983 (m), 830 (m), 794 (s), 771 (s).

Poly[(hexadecamethyloctasilanylene)-4,3′′′′′-di-*n*-octylsexithiophene] (13d; p-$T_6Oct_2Si_8Me_{16}$). The reaction was performed using 1,8-bis(2-thienyl)hexadecamethyloctasilanylene (1.26 g, 2 mmol) in THF and gave 3.7 g (78%) of **13d** as a red solid. ^1H NMR δ 0.15−0.19 (m, 36H, $SiCH_3$), 0.43 (s, 12H, $SiCH_3$), 0.89 (bs, 6H, CH_3), 1.30 (m, 20H, CH_2), 1.67 (m, 4H, β-CH_2), 2.77 (m, 4H, α-CH_2), 7.02 (m, 4H), 7.06 (d, 2H), 7.12 (d, 2H), 7.21 (d, 2H) ppm. ^{13}C NMR δ −5.4, −4.4, −4.2, −1.8 ($SiCH_3$), 14.0 (CH_3), 22.6 (α-CH_2/Oct), 29.2, 29.3, 29.4, 30.4, 31.8 (CH_2), 123.8, 124.9, 126.2, 126.6, 134.8 (CH), 129.1, 135.1, 135.4, 136.7, 139.4, 140.5, 142.0 (C) ppm. ^{29}Si NMR δ −43.0, −38.9, −37.7, −20.1 ppm. UV λ_{max} = 424 nm, ϵ = 46200. IR (film on KBr pellet) 2951 (s), 2926 (s), 2854 (m), 1635 (s), 1457 (w), 1436 (w), 1403 (w), 1247 (m), 1068 (w), 982 (w), 832 (m), 793 (m), 759 (s).

6.5. Model Compounds. 5,5′-Bis(trimethylsilyl)-2,2′-bithiophene (14a; $Me_3SiT_2SiMe_3$). TMEDA (2.45 g, 20 mmol) was added to a solution of *n*-BuLi (8 mL, 20 mmol). After 5 min the clear warm solution was cooled to −10 °C and 2,2′-bithiophene (3.36 g, 20 mmol) was added dropwise, while the temperature was kept between 0 and 10 °C. After 5 min, pentane (5 mL) was added and stirring was continued during another 5 min. The reaction mixture was cooled to 0 °C after

Scheme 6



4,5: v = 0 and 1

14a-b: v = 0; y = 1 and 2
15a-b: v = 1; y = 1 and 2

which a second equivalent of *n*-BuLi (8 mL, 20 mmol) was added. The white suspension dissolved between 20 and 25 °C. Upon slow heating to 30 °C, a white suspension was formed again, which was refluxed for 30 min and subsequently cooled to 0 °C. Ether (50 mL) was added, followed by an excess of chlorotrimethylsilane (5 g, 46 mmol). The temperature was raised to 30 °C and stirring was continued for 1 h. The reaction mixture was poured into 50 mL of cold water and extracted with ether (2 × 35 mL). The combined organic layers were washed with 5% NaCl solution (25 mL), dried (MgSO$_4$), and filtered, and the solvents were removed by evaporation under reduced pressure. Kugelrohr distillation (190 °C, 1 mm Hg) of the crude reaction product provided 4.22 g (68%) of the title product as a white solid, mp 91–92 °C. ^{1}H NMR δ 0.34 (s, 18H, SiMe$_3$), 7.13 (d, 2H, ^3J = 3.5, H-4), 7.23 (d, 2H, H-3). ^{13}C NMR δ −0.2 (Me), 125.0 (^1J = 165.2, ^2J = 7.2, C-3), 134.6 (^1J = 166.0, ^2J = 4.8, C-4), 139.8 (C-5), 142.4 (C-2). ^{29}Si NMR δ −6.6 ppm. IR 2953 (m), 1423 (m), 1249 (s), 1198 (m), 1074 (m), 988 (s), 874 (s), 840 (s), 798 (s), 754 (s). MS *m/e* (rel intensity) 310 (M$^+$, 100), 295 (M$^+$ − Me, 90), 73 (SiMe$_3$, 31). Exact mass determination calcd for $C_{14}H_{22}S_2Si_2$: 310.070. Found: 310.071.

5,5′-Bis(pentamethyldisilanyl)-2,2′-bithiophene (14b; Me$_5$Si$_2$T$_2$Si$_2$Me$_5$). The reaction was performed on a 10 mmol scale, following the same procedure as applied for Me$_3$SiT$_2$SiMe$_3$, using 2,2′-bithiophene (1.66 g, 10 mmol). Kugelrohr distillation (190 °C, 0.01 mmHg) and subsequent crystallization from chloroform/methanol provided 1.82 g (43%) of the title product as a white solid, mp 77–78 °C. ^{1}H NMR δ 0.12 (s, 18H, SiMe$_3$), 0.38 (s, 12H, SiMe$_2$), 7.07 (d, 2H, ^3J = 3.5, H-4), 7.24 (d, 2H, H-3). ^{13}C NMR δ −2.9/−2.5 (Me), 124.9 (C-3), 134.7 (C-4), 138.5 (C-5), 142.2 (C-2). ^{29}Si NMR δ −24.0/−19.2 ppm. IR 2950 (m), 1420 (w), 1242 (m), 1193 (w), 1070 (w), 986 (m), 873 (w), 832 (m), 793 (s), 763 (w), 725 (w). MS *m/e* (rel intensity) 426 (M$^+$, 59), 353 (M$^+$ − SiMe$_3$, 82), 73 (SiMe$_3$, 100). Exact mass determination calcd for $C_{18}H_{34}S_2Si_4$: 426.118. Found: 426.118.

5,5″-Bis(trimethylsilyl)-2,2′:5′,2″-terthiophene (15a; Me$_3$SiT$_3$SiMe$_3$). *n*-BuLi (2.0 mL, 3.2 mmol) was added dropwise to a solution of 2,2′:5′,2″-terthiophene (0.80 g, 3.2 mmol) in THF (10 mL), keeping the temperature below −30 °C. After complete addition and stirring for 15 min, *n*-BuLi (2.0 mL, 3.2 mmol) was added dropwise at −40 °C. The temperature rose and stirring was continued for 30 min at −10 to 0 °C. Chlorotrimethylsilane (1.1 g, 10 mmol) was added in one portion at −40 °C. The mixture was allowed to warm to room temperature slowly before being poured into water (50 mL). The mixture was extracted with ether (3 × 100 mL), the combined organic layers were washed with 5% NaCl solution (50 mL), dried (MgSO$_4$), and filtered, and the solvents were removed by evaporation under reduced pressure. Column purification (Kieselgel-60, CH$_2$Cl$_2$/pentane = 1:10) of the crude reaction product provided 0.98 g (78%) of the title product as a light-green solid, mp 121–123 °C. ^{1}H NMR δ 0.32 (s, 18H, SiMe$_3$), 7.08 (s, 2H, s, H-3′/4′), 7.13 (d, 2H, ^3J = 3.4, H-4), 7.22 (d, 2H, H-3). ^{13}C NMR δ −0.2 (Me), 124.3 (^1J = 167.6, ^2J = 4.8, C-3′/4′), 124.8 (^1J = 166.0, ^2J = 6.4, C-3), 134.7 (^1J = 166.0, ^2J = 4.8, C-4), 136.2 (C-2′), 139.9 (C-5), 142.0 (C-2). ^{29}Si NMR δ −6.4 ppm. IR 2953 (m), 1430 (m), 1247 (m), 1200 (w), 1070 (m), 987 (s), 912 (w), 839 (s), 795 (s), 756 (m). MS *m/e* (rel intensity) 392 (M$^+$, 100), 377 (M$^+$ − Me, 61). Exact mass determination calcd for $C_{18}H_{24}S_3Si_2$: 392.057. Found: 392.058.

5,5″-Bis(pentamethyldisilanyl)-2,2′:5′,2″-terthiophene (15b; Me$_5$Si$_2$T$_3$Si$_2$Me$_5$). The reaction was performed on a 5.0 mmol scale following the same procedure as applied for Me$_3$SiT$_3$SiMe$_3$. Kugelrohr distillation (220 °C, 0.01 mmHg) and subsequent crystallization from chloroform/methanol provided 1.42 g (56%) of the title product as a green solid, mp 131–133 °C. ^{1}H NMR δ 0.11 (s, 18H, SiMe$_3$), 0.39 (s, 12H, SiMe$_2$), 7.08 (d, 2H, ^3J = 3.5, H-4), 7.08 (s, 2H, H-3′/4′), 7.23 (d, 2H, ^3J = 3.5, H-3). ^{13}C NMR δ −2.9/−2.5 (Me), 124.2 (C-3′/4′), 124.8 (C-3), 134.7 (C-4), 136.1 (C-2′), 138.9 (C-5), 142.0 (C-2). ^{29}Si NMR δ −23.9/−19.2 ppm. IR 2949 (m), 1424 (w), 1245 (s), 1190 (w), 1068 (m), 981 (s), 891 (w), 832 (s), 789 (s), 726 (w). MS *m/e* (rel intensity) 508 (M$^+$, 100), 435 (M$^+$ − SiMe$_3$, 46), 378 (M$^+$ − Si$_2$Me$_5$, 42), 305 (M$^+$ − Si$_3$Me$_8$, 23), 73 (SiMe$_3$, 54). Exact mass determination calcd for $C_{22}H_{36}S_3Si_4$: 508.106. Found: 508.105.

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(42) The resonances of the CH_3 groups in the ^1H and ^{13}C NMR spectra contained twice to four times as many signals as expected. The ^{29}Si NMR showed eight resonances instead of the expected four. A possible explanation is the presence of conformational isomers due to π-stacking of the thiophene groups.

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