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Photophysics of Main-Chain Polychromophores Prepared by Acyclic Diene Metathesis Polymerization

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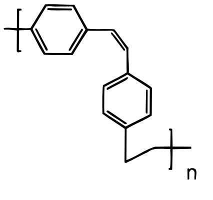
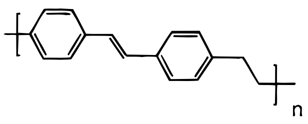
ABSTRACT: A series of bis(vinylthienyl)silane monomers were prepared by reaction of 2 equiv of (vinylthienyl)lithium or (vinylthienyl)magnesium bromide with different dichlorosilicon dialkyls. The monomers react with the Schrock initiator Mo(NAr)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$ (Ar = 2,6-diisopropylphenyl), via the acyclic diene metathesis polymerization (ADMET) mechanism, to give poly(silanyl−dithienylethene) derivatives in excellent yield. GPC data suggest that the resulting polymers have short repeat sequences. Interchromophore cooperativity is evident, as a low energy emission, for polymer structures that have smaller side groups. This phenomenon is similar to the chromophore cooperativity observed in polymers containing stilbene fragments along the backbone.

Introduction

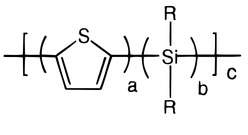
Polymers containing a high content of chromophores are interesting for a variety of reasons.[1] They have been investigated for potential use in electron and energy transfer. “Photon-harvesting” polymers are known to collect energy in the form of a photon and transfer this excitation to fluorophores with lower energy excited states. Synthetic polymers of this type mimic several of the steps characteristic of photosynthesis.[2]

Because chromophores in a polymer chain are connected to each other, their local concentration is high and complex photophysical behavior is often observed. Polymers with structures that have pendant chromophores are well studied. Excimer (excited state dimer) emission often dominates emission spectra.[1a,3,4] Main-chain polychromophores have received less attention. This is especially true for structures that contain a large percentage of chromophores in the backbone because of their low solubility and more difficult synthesis.[5] In situations where the spacer unit between chromophores is relatively short, the emission data suggest chromophore−chromophore interactions in the excited state. For example, in the case of poly(paracyclophene) derivatives, aggregation of their constituent stilbene chromophores, together with efficient energy transfer, results in blue light emission.[5,6]


cis-poly(paracyclophene)


trans-poly(paracyclophene)

Conjugated polymers can be considered as the extreme case of main-chain polychromophores where no linkage exists between chromophore units.[7] These materials have found considerable recent attention as the emissive layer in organic light-emitting devices.[8,9] Electroluminescence from a polymer containing well-defined fluorophores linked by flexible spacers has also been demonstrated.[10] This structure opens the possibility to control the emission color by choice of chromophore.[11,12] Polymers utilizing silicon-based spacers have also been reported to display electroluminescence.[13] Light-emitting diodes made using poly[(silanylene)thiophene]s emit in the visible region of the spectrum.[13] Absorption and emission data suggest only weak σ-conjugation coupling between chromophores by way of the silicon linker.[13,14]



poly[(silanylene)thiophene]

In this paper we present the synthesis of poly [(silanylene)dithienylethylene] derivatives *via* the acyclic diene metathesis (ADMET) polymerization method. These polymers consist of an alternating structure of dithienylethene chromophores and silanylene linkers. We are interested in understanding how the molecular structure of these polymers affects interchromophore cooperativity.

Results and Discussion

Monomer Synthesis. The general strategy for monomer synthesis is shown in Scheme 1. For the ADMET condensation reaction to proceed, two terminal vinyl functionalities are required on both sides of the core structure. Monomer synthesis begins by olefination of 5-bromothiophenecarboxaldehyde (**1**)[15] using Wittig chemistry to give vinylthienyl bromide (**2**),[16] which can be purified by distillation in 60% yield. The Grignard derivative **3** is formed by reacting **2** with Mg in THF at room temperature. Quenching with $^1/_2$ equiv of Me$_2$SiCl$_2$ gives, after chromatography, bis(vinylthienyl)dimethylsilane (**6**), in 30% yield. It is best to store **6** in the presence of a radical scavenger, such as 4-*tert*-butylcatechol, or at −30 °C to prevent radical polymerization. The reaction of **3** with Et$_2$SiCl$_2$ produces only the monoalkylated product. Reacting excess **3** with MeSiCl$_3$ gives bis(vinylthienyl)chloromethylsilane (**5**). The remaining chloride does not exchange with **3** even after heating for 12 h. Reaction of **5** with PhMgBr gives bis(vinylthienyl)phenylmethylsilane (**8**) in 30% yield while BuMgBr with **5** gives bis(vinylthienyl)butylmethylsilane (**7**) in 30% yield.

The lithium analog of **3** provides a more reactive species.[17] Treating **2** with *t*-BuLi at −78 °C furnishes

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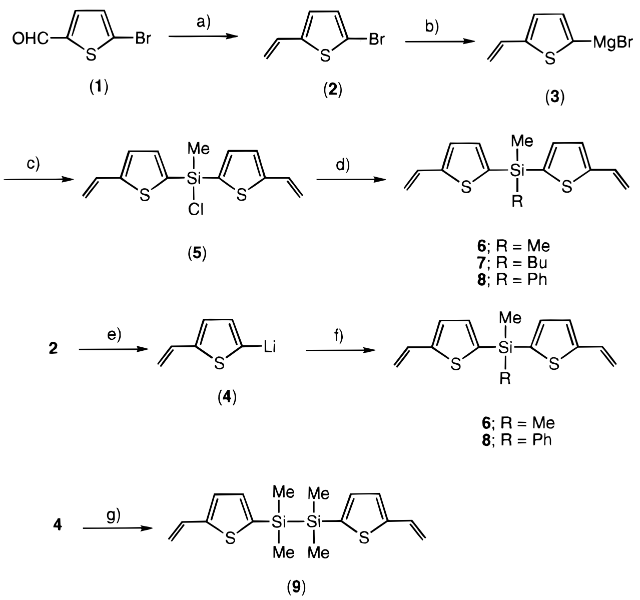
Scheme 1[a]

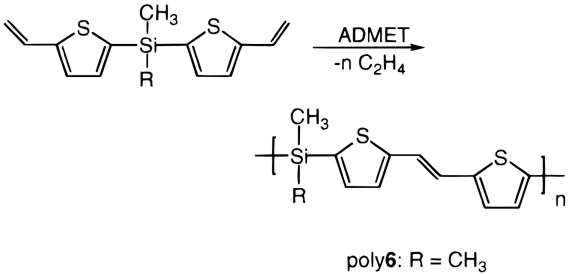


[a] Key: $MePPh_3Br$, K_2CO_3; (b) Mg, THF; (c) 1/2 $MeSiCl_3$; (d) MeMgBr for **6**, BuMgBr for **7**, PhMgBr for **8**; (e) *tert*-BuLi, THF, −78 °C; (f) $^1/_2$ Me_2SiCl_2 for **6**, $^1/_2$ $PhMeSiCl_2$ for **8**; (g) $Me_4Si_2Cl_2$.

(vinylthienyl)lithium (**4**) quantitatively. However, this lithium species is thermally unstable and is best used immediately. Quenching **4** with $MePhSiCl_2$ gives **8** in 62% yield while Me_2SiCl_2 gives **6** in 82% yield. Although the lithium approach affords the target monomers in two less steps and in higher yields, the Grignard method offers more synthetic flexibility.

The disilane monomer bis(vinylthienyl)tetramethyldisilane (**9)** was also prepared by reaction of two equiv **4** with tetramethyldichlorodisilane (see Scheme 1). Purification by chromatography gives **9** as a viscous oil in 50% yield. To minimize radical polymerization, **9** is stored as a chloroform solution at −30 °C.

Polymerization. The procedure for ADMET polymerization has been described elsewhere in detail.[18,19] In our case we relied on the molybdenum complex $Mo(NAr)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$ (Ar = 2,6-diisopropylphenyl)[20] to initiate the reaction (eq 1).



(1)

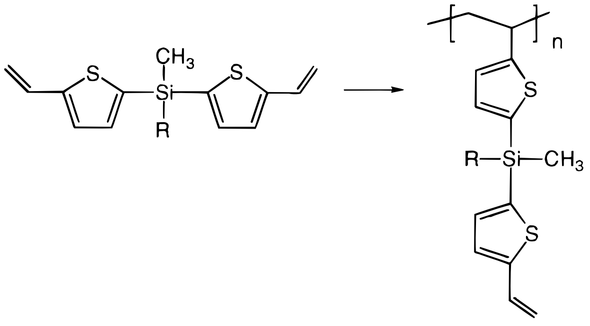
poly**6**: R = CH_3
poly**7**: R = Bu
poly**8**: R = Ph

A recurring unwanted side reaction encountered was free radical polymerization (eq 2). This complication can be minimized by performing the ADMET polymerizations in toluene at room temperature under dynamic vacuum. Neat monomer conditions favor a larger percentage of the free radical product (estimated at 40% by GPC in the worst case). Previous work has also shown that the styryl end groups are susceptible to free radical addition under ADMET conditions.[21] Ethylene release is evident during the first 20 min of the polymerization and slows down as the reaction progresses. Quenching is carried out by exposure to air and the polymers are isolated by precipitation into methanol. Analysis by ^{13}C and ^1H NMR spectroscopy reveals that in all cases the polymer obtained is >95% trans stereoregular.

Table 1. GPC and UV−Vis Absorption Data[a]

Poly no.	M_n[b]	M_n/M_w	*n*(GPC)	*n*(NMR)	λ_{max} (nm)
6	3100	1.4	11	10	365
7	6700	2.4	22	20	366
8	5300	2.9	16	10	365
9[c]	6800	1.4	21		374

[a] All GPC results are calibrated against polystyrene standards. [b] M_n = number average molecular weight. [c] Multimodal distribution.



(2)

The polymer structures resulting from ADMET and radical polymerizations have different absorption spectra. The ADMET product has a more conjugated structure and absorbs at λ_{max} = 365 nm. In comparison, the polymer from free radical polymerization absorbs at λ_{max} = 255 nm. By GPC, the radical polymerization product appears as a high molecular weight component (M_n = 11 900).

The molecular weights of the ADMET products are not high. GPC results, shown in Table 1, suggest that these materials are better viewed as oligomers rather than high molecular weight polymers. It should be noted that highly concentrated reaction conditions, or neat monomer, maximize the molecular weight in ADMET reactions.[19] For the bis(vinylthienyle)silane monomers discussed here, this is not possible because of the free radical polymerization side reactions described above and also because the low solubility of the resulting polymers.

In all cases, the ^1H and ^{13}C NMR data are consistent with the proposed structure. Most indicative is the disappearance of three terminal olefin signals of the monomer at 5.18, 5.63, and 6.84 ppm and the emergence of the signal at 7.07 ppm corresponding to the olefinic bridge. From the integration of this resonance relative to residual terminal groups we can estimate the number of repeat units (*n*) for the different polymers,[22] as shown in Table 1.

Poly**9**, containing disilane bridging units, can be prepared similarly. It decomposes upon exposure to air or light. Proton NMR spectra of the sample taken after 1 day shows decomposition of the dithienylethene structure. The broad aromatic multiplets of the polymer split into many sharp peaks and the broad methyl singlet at 0.38 ppm breaks up into several narrow resonances. Decomposition of poly**9** is most likely a result of the weak Si−Si bonds along the polymer backbone. Other polymers with disilane linkers show similar instability.[23]

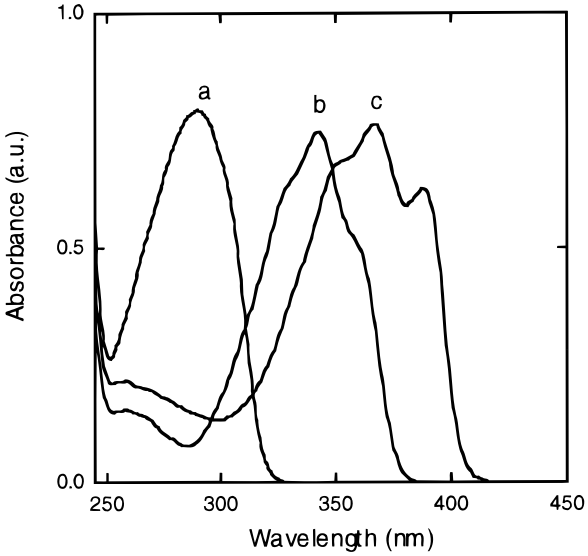


Figure 1. UV−Vis absorption spectra of (a) monomer **8**, (b) *trans*-dithienylethene, and (c) poly**8**.

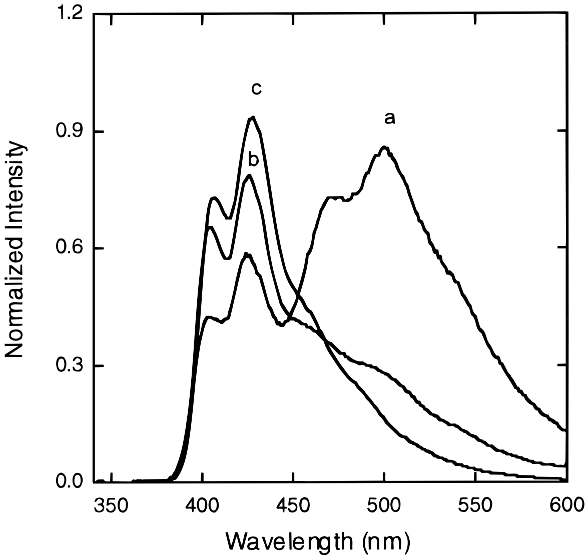


Figure 2. Fluorescence emission spectra ($\lambda_{\text{excitation}} = 310$ nm) of (a) poly**6,** (b) poly**7**, and (c) poly**8**.

Absorption and Emission Spectra. The absorption spectra of all monomers are similar, indicating that the silicon substituents exert little perturbation. After polymerization, absorption maxima is red shifted relative to the monomer, consistent with the expected increase of delocalization with formation of the dithienylethene structure. Figure 1 compares the UV/vis spectrum of **8** ($\lambda_{\max} = 290$ nm) against that of *trans*-dithienylethene ($\lambda_{\max} = 342$ nm) and poly**8**.[24,25] The absorption of poly**8** is approximately 25 nm red-shifted relative to that of *trans*-dithienylethene, probably as a result of silicon substitution and partial delocalization along the chain.

Emission data for poly**6**, poly**7**, and poly**8** in $CHCl_3$ at room temperature are shown in Figure 2. For poly**8**, the emission maximum at 426 nm ($\lambda_{\text{exc}} = 350$ nm) is red shifted relative to that of *trans*-dithienylethene ($\lambda_{\text{em}} = 401$ nm) by approximately 25 nm. Therefore, the polymer structure exerts little influence other than what would be expected by silicon substitution. In the case of poly**6**, a broad emission centered roughly at 500 nm is observed which is significantly red-shifted relative to that of dithienylethene. Poly**7** appears to be an intermediate case with a broad shoulder extending from the monomer emission band to the low-energy region. (All spectra in Figure 2 are approximately 10^{-4} M of polymer in $CHCl_3$.)

Table 2. Parameters for Exponential Fits after Deconvolution from the Instrument Impulse Response for the Fluorescence Decay Curves of Thiophene Polymers ($\lambda_{\text{ex}} = 350$ nm)

material	λ_{em} (nm)	t_1[a] (ps)	A_1[a] (%)	t_2 (ps)	A_2 (%)	t_3 (ps)	A_3 (%)	χ^2
Poly**6**	380	17	37	260	58	1100	5	0.90
	400	22	38	260	58	1000	4	1.3
	425	20	36	270	58	1300	7	1.2
	465	22	26	310	50	1100	24	1.3
	500	86	19	550	71	1900	10	1.7
	540	43	11	510	73	1500	16	1.7
	580	62	10	530	73	1600	17	1.7
Poly**7**	380	55	35	300	51	490	14	1.3
	400	69	44	320	46	480	9	1.1
	420	53	32	300	59	650	8	1.0
	460	58	27	330	56	910	17	2.2
	500	74	18	390	50	1010	32	1.3
	550	140	21	440	46	1100	33	1.4
Poly**8**	380	47	25	330	68	690	6	0.90
	400	120	38	390	62			1.3
	420	210	62	500	38			1.6
	460	240	63	680	37			2.1
	500	260	50	780	49			1.8
	550	290	40	850	62			1.5
dithienylethene	400							1.1
	450							1.1

[a] The table presents the results of four exponential fits to the luminescence decay. The values of t_{1-4} denote the time constants of the exponentials, and the values of A_{1-4} denote their relative weights. The absence of entries for the higher variables means that an acceptable fit was obtained with two or three exponentials.

The most noteworthy feature of the fluorescence spectra in Figure 2 is the low-energy band that appears as the steric bulk on the silicon linker decreases.[4] The different properties of poly**6** and poly**7** suggest that the new fluorescent species is a result of chromophore close proximity. The larger, more soluble, butyl substituents discourage chromophore close proximity and extend the polymer chain in good solvents. Expanded polymer dimensions increase the average interchromophore distance. We refer to the low-energy component in polythienylethene as "aggregate" fluorescence to emphasize its multichromophore nature (two or greater) and to distinguish it from normal excimer fluorescence, observed in pendant structures.[4,26] Importantly, because dilution of poly**6** solutions only decreases the intensity of the entire spectrum while keeping the ratio of the two bands constant, we can infer that aggregation is intramolecular.[27]

Fluorescence lifetimes were also measured using the technique of time-correlated single photon counting (Table 2). For all polymers, the decays are slower than that observed for the parent dithienylethene. It is also interesting to note that the low-energy emission band of poly**6** has a longer lifetime than the high-energy component. This difference is especially obvious when the two decay rates are overlaid as in Figure 3. Fitting the measured decay profiles required multiexponential functions, and some of these kinetic parameters are listed in Table 2. Note that the high-energy envelope is dominated by a fast subnanosecond component and shows more heterogeneity. The structured peaks within each band are described by identical functions which suggest that they are due to vibronic structure.

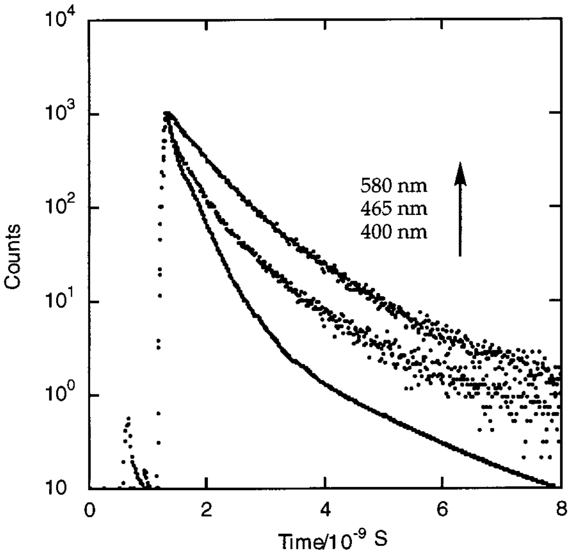


Figure 3. For poly**6** in $CHCl_3$, fluorescence lifetime measurements monitored at different wavelengths.

Conclusion

A class of alternating copolymers incorporating silane and thienylethene functionalities can be accessed via ADMET polymerization. Photophysical measurements of these polymers reveal that their fluorescent properties are different from that of noninteracting dithienylethene chromophores and are analogous to those observed in poly(paracyclophene)s. These studies disclose that emission from aggregated chromophores may be a fairly general phenomenon in main-chain polymers provided that these chromophores are allowed to approach each other. Controlling stilbenoid chromophore interactions in polymers could potentially be useful in modulating their emission frequencies without changing the basic molecular structure of the chromophore. Studies on how the geometry, chain length, and solvent polarity affect the interactions of chromophore cooperativity are currently underway.

Experimental Section

General Details. All manipulations involving organometallic reagents were carried out using either high-vacuum or glovebox techniques as described previously.[28] ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer at 400.1 MHz and 100.6 MHz, respectively, UV–vis absorption spectra on either a Perkin-Elmer Lambda 19 spectrophotometer or a Hewlett-Packard 8452A diode array spectrophotometer, and photoluminescence spectra on a Spex Fluorolog 2 spectrometer. The experimental setup for the time-correlated, single photon counting experiments has been described previously.[5] Solid-state spectra of polymers were measured on films cast on quartz plates. Molecular weight determinations are relative to polystyrene standards (Tosoh Corporation) and are based on separations by gel permeation chromatography (GPC) of chloroform solutions of the polymers in question; the standards ranged in molecular weight from 1051 to 1.9×10^5. The instrument employed was a Waters HPLC-GPC system equipped with a Model 600E controller and a Model 996 photodiode array detector, and it was loaded with Shodex columns (K-800P, 806, 804, 802, KF-801) arranged in series. The chloroform was Baker HPLC grade and was filtered through a Millex-SR 0.5-μm filter before use. High-resolution mass spectrometry was performed by the Center for Mass Spectrometry at the University of Nebraska–Lincoln. Toluene for polymerizations was vacuum distilled from benzophenone ketyl immediately before use. The silica gel for column chromatography was 230–400 mesh and was purchased from EM Science. Small amount of free radical inhibitor, 4-*tert*-butylcatechol was used for monomer storage. The molybdenum catalyst[29] and *trans*-dithienylethene[25] were prepared according to literature procedures. 5-Bromo-2-thiophenecarboxaldehyde, dichlorodimethylsilane, and dichlorotetramethylsilane were purchased from Lancaster or Aldrich Co. and used as received.

Vinylthienyl Bromide (2). A mixture of 5-bromo-2-thiophenecarboxaldehyde (2 g, 10.5 mmol), methyltriphenylphosphonium bromide (3.38 g, 9.5 mmol), and K_2CO_3 (2 g, 14.5 mmol), in 60 mL 1,4-dioxane and 0.5 mL H_2O, was refluxed under vigorous stirring for 48 h. The resulting suspension was poured into water and extracted with hexanes. The combined organic layers were washed with brine and dried with $MgSO_4$. The solvent was removed and the residue was distilled under reduced pressure to give 1.0 g of pure yellow liquid (yield, 50%). ^1H NMR ($CDCl_3$) is consistent with literature values:[16] δ 6.90 (d, $J = 3.4$ Hz, 1H), 6.69 (d, $J = 3.4$ Hz, 1H), 6.66 (dd, $J = 17.4$ Hz, 10.1 Hz, 1H), 5.47 (d, $J = 17.4$ Hz, 1H), 5.14 (d, $J = 10.1$ Hz, 1H).

(Vinylthienyl)magnesium Bromide (3). Fresh magnesium turnings (0.22 g, 9.05 mmol) were activated with dibromoethane in a small amount of THF. To this mixture was added a solution of **2** (0.95 g, 5 mmol) in THF (15 mL) dropwise. After the addition, the mixture was stirred at room temperature overnight. Since no appropriate indicator was found to determine the Grignard concentration, the resulting dark solution was used in next step without titration.

(Vinylthienyl)lithium (4). *tert*-Butyllithium (0.75 mL, 1.7 M in Et_2O) was added to **2** dropwise (0.2 g, 1.06 mmol) at −78 °C. The mixture was allowed to stir at this temperature for an hour, and the resulting yellow solution was used directly in the next step of reaction.

Bis(vinylthienyl)chloromethylsilane (5). Trichlorodimethylsilane (0.19 g, 1.47 mmol) was added to a THF solution of **3** freshly made from vinylthienyl bromide (0.7 g, 3.7 mmol) and magnesium (0.26 g, 10.7 mmol). The mixture was stirred at room temperature for an hour and heated to 50 °C overnight.

Bis(vinylthienyl)dimethylsilane (6). Method a. Dichlorodimethylsilane (0.19 g, 1.47 mmol) was added to a THF solution of **3** freshly made from vinylthienyl bromide (0.7 g, 3.7 mmol) and magnesium (0.26 g, 10.7 mmol). The mixture was stirred at room temperature for an hour and refluxed overnight. After solvent removal, the residue was chromatographed on silica gel with hexanes as solvent to give 0.1 g of the product as a colorless liquid (yield, 25%).

Method b. Methylmagnesium bromide (2.2 mL, 3 M in Et_2O) was added to **5** prepared from vinylthienylbromide (0.7 g, 3.7 mmol). The mixture was refluxed for 10 h. The crude product was purified in a manner similar to that of method a.

Method c. Dichlorodimethylsilane (0.19 g, 1.47 mmol) was added slowly to the THF solution of **4** at −78 °C. The mixture was allowed to warm to room temperature over a period of 10 h. The solvent was then removed, and the residue was chromatographed on silica gel with hexanes to give 0.12 g of **6** (yield, 82%). ^1H NMR ($CDCl_3$): δ 7.16 (d, $J = 3.6$ Hz, 2H), 7.03 (d, $J = 3.6$ Hz, 2H), 6.82 (dd, $J = 17.2$, 10.6 Hz, 2H), 5.60 (d, $J = 17.2$ Hz, 2H), 5.16 (d, $J = 10.6$ Hz, 2H), 0.61 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 149.1, 136.6, 135.8, 129.6, 127.1, 114.1, −0.35. HREI: calcd for $C_{14}H_{16}S_2Si$, 276.0463; found, 276.0461.

Bis(vinylthienyl)butylmethylsilane (7). Butylmagnesium bromide (5 mL, 2.0 M in Et_2O) was added to **5** prepared from methyltrichlorosilane (0.25 g, 1.67 mmol). The mixture was heated to 60 °C for 12 h. The workup procedure is similar to that used for **6.** ^1H NMR ($CDCl_3$): δ 7.17 (d, $J = 3.5$ Hz, 2H), 7.04 (d, $J = 3.5$ Hz, 2H), 6.83 (dd, $J = 17.6$, 10.8 Hz, 2H), 6.62 (d, $J = 17.6$ Hz, 2H), 5.15 (d, $J = 10.8$ Hz, 2H), 1.41 (m, 4H), 1.06 (m, 2H), 0.89 (t, $J = 7.6$ Hz, 3H), 0.61 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 149.1, 136.1, 135.8, 129.6, 127.2, 114.1, 29.8, 25.9, 16.0, 13.8, −2.2. HREI: calcd for $C_{17}H_{22}SiS_2$, 318.0957; found, 318.0927.

Bis(vinylthienyl)phenylmethylsilane (8). Phenylmagnesium bromide (5 mL, 2.0 M in Et_2O) was added to **5** prepared from methyltrichlorosilane (0.25 g, 1.67 mmol). The mixture was heated to 60 °C for 12 h. The workup procedure is same as that used for **6.** Method c from **6** was used. Dichlorodimethylphenylsilane (0.081 g, 0.42 mmol) was added slowly to a THF solution of **4** at −78 °C. The mixture was allowed to warm up to room temperature over a period of 10 h. The solvent was removed, and the residue was chromatographed on silica gel with hexanes to give 0.11 g of liquid (yield, 62%). ^{1}H NMR ($CDCl_3$): δ 7.63 (m, 2H), 7.40 (m, 3H), 7.20 (d, J = 3.2 Hz, 2H), 7.06 (d, J = 3.2 Hz, 2H), 6.82 (dd, J = 17.6, 10.8 Hz, 2H), 5.63 (d, J = 17.6 Hz, 2H), 5.16 (d, J = 10.8 Hz, 2H), 0.89 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 149.9, 137.5, 135.3, 134.8, 134.6, 130.1, 129.6, 128.1, 127.2, 114.5, −1.28. HREI: calcd for $C_{19}H_{18}SiS_2$, 338.0619; found, 338.0619.

Bis(vinylthienyl)tetramethyldisilane (9). Dichlorotetramethylsilane (0.08 g, 0.43 mmol) was added slowly to the THF solution of **4** prepared from **2** (0.2 g, 1.06 mmol) at −78 °C. The mixture was allowed to warm up to room temperature over a period of 10 h. The solvent was removed, and the residue was chromatographed on silica gel with hexanes to give 0.06 g of the product as a colorless liquid (yield, 50%). ^{1}H NMR ($CDCl_3$): δ 7.02 (s, 4H), 6.83 (dd, J = 17.2, 10.8 Hz, 2H), 5.60 (d, J = 17.2 Hz, 2H), 5.13 (d, J = 10.8 Hz, 2H), 0.40 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 148.4, 137.5, 135.0, 129.7, 127.3, 113.6, −2.8. HREI: calcd for $C_{16}H_{22}Si_2S_2$, 334.0702; found, 334.0731.

Poly[5-(dimethylsilanylene)dithienylethylene] (poly6). In a nitrogen-filled glovebox, a round-bottom flask equipped with a vacuum line adapter was charged with **6** (120 mg, 0.435 mmol), molybdenum catalyst (12 mg, 0.016 mmol), and 8 mL of dry toluene. The apparatus was opened to vacuum intermittently and stirred at room temperature for 48 h. The reaction was quenched by exposing to air. The polymer was isolated by precipitation into hexanes and collected by centrifugation. ^{1}H NMR ($CDCl_3$): δ 7.17 (m, 2H), 7.07 (m, 4H), 0.61 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 147.2, 135.4, 126.2, 125.2, 124.4, 123.2, −0.4.

Poly[5-(butylmethylsilanylene)dithienylethylene] (poly7). The preparation procedure is similar to that of poly**6**. ^{1}H NMR ($CDCl_3$): δ 7.17 (d, 2H), 7.09 (m, 4H), 1.43 (m, 4H), 1.06 (m, 2H), 0.86 (m, 3H), 0.60 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 148.4, 136.7, 127.7, 126.2, 124.4, 122.3, 26.4, 25.9, 15.9, 13.7, −2.3.

Poly[5-(phenylmethylsilanylene)dithienylethylene] (poly8). The preparation procedure is similar to that of poly**6**. ^{1}H NMR ($CDCl_3$): δ 7.60 (br d, 3H), 7.38 (br d, 2H), 7.18 (br s, 2), 7.07 (s, 4H); 0.87 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 149.1, 137.7, 135.1, 134.7, 130.1, 128.1, 127.2, 122.0, −1.4.

Poly[5-(tetramethylsilanylene)dithienylethylene] (poly9). The preparation procedure is similar to that of poly**6**. ^{1}H NMR ($CDCl_3$): δ 7.24 (s, 2H), 7.05 (m, 4H), 0.38 (br s, 12H). Due to instability, the ^{13}C NMR data could not be obtained.

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References and Notes

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