Silole-Containing π-Conjugated Systems. 3.[1] A Series of Silole–Thiophene Cooligomers and Copolymers: Synthesis, Properties, and Electronic Structures

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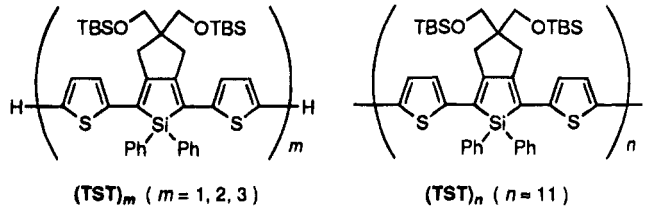
Received May 9, 1995; Revised Manuscript Received September 20, 1995[⊗]

ABSTRACT: A series of silole (silacyclopentadiene)–thiophene copolymers, silole:thiophene 1:2, 1:3, and 1:4 copolymers, have been synthesized by palladium-catalyzed cross-coupling reactions. Silole–thiophene alternating 1:1 cooligomers (up to a seven-ring system) have also been prepared as models of their copolymers by nickel-promoted intramolecular cyclizations of the corresponding thiophene–1,6-heptadiyne cooligomers with hydrodisilanes. The UV–visible absorption data show that an increase in the silole content causes bathochromic shifts. In contrast, the conductivity tends to become higher with the higher thiophene content, the conductivity reaching up to 2.4 S cm^{-1} upon doping with iodine. Theoretical studies on the electronic structures of silole–thiophene cooligomers suggest that the unusual long absorptions observed for silole–thiophene mixed systems are mainly ascribed to the unique electronic structures of the silole rings.

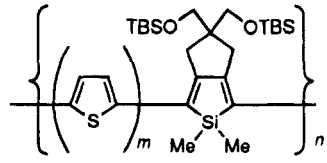
Introduction

The synthesis of copolymers between electron-donating rings and electron-accepting rings is promising for development of novel π-electronic organic materials.[1a,2-4] Such combinations may cause unusual electronic structures in the main chain, such as narrow band gaps.[3,4]

We have recently reported the synthesis of alternating cooligomers and copolymer between thiophenes as the electron-donating part and substituted siloles (silacyclopentadienes) as the electron-accepting part.[1a] The electron-accepting properties of the silole ring have been demonstrated by reduction with alkali metals.[5] The cooligomers, $(TST)_m$ (m = 1, 2, 3), and the copolymer, $(TST)_n$ ($n \approx 11$), indeed show large red shifts in electronic spectra compared with oligothiophenes and polythiophenes: hereafter thiophene and bicyclic 1,1-diphenylsilole are abbreviated to T and S, respectively (see Chart 1). For example, $(TST)_n$ has absorption maxima in chloroform at 594 and 615 nm, more than 150 nm longer than that (438–450 nm) of the well-defined poly(3-alkylthiophene).[6] These findings indicated the formation of unusual electronic structures in the TST system. To obtain more detailed information about the electronic structures, we have now studied a series of silole–thiophene mixed systems **1** whose silole–thiophene ratios are varied from 1:1 to 1:4. Herein we describe the synthesis of the copolymers **1**, their UV–vis absorptions, electrical conductivities, and theoretical studies.



$(TST)_m$ (m = 1, 2, 3) $(TST)_n$ ($n \approx 11$)



1

(m = 1, 2, 3, 4)

(TBSO = *t*-butyldimethylsiloxy)

Results and Discussion

Monomer Synthesis. In this study we have chosen a 1,1-dimethylsilole (abbreviated to S′) in place of 1,1-diphenylsilole (S) as the silole part, in order to improve the solubility of the polymers (Chart 1).

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1995.

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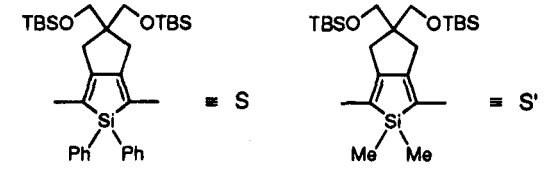
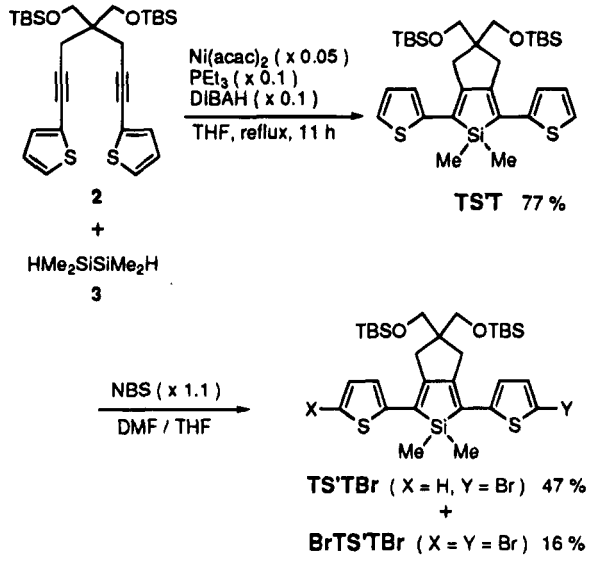
Chart 1



Scheme 1

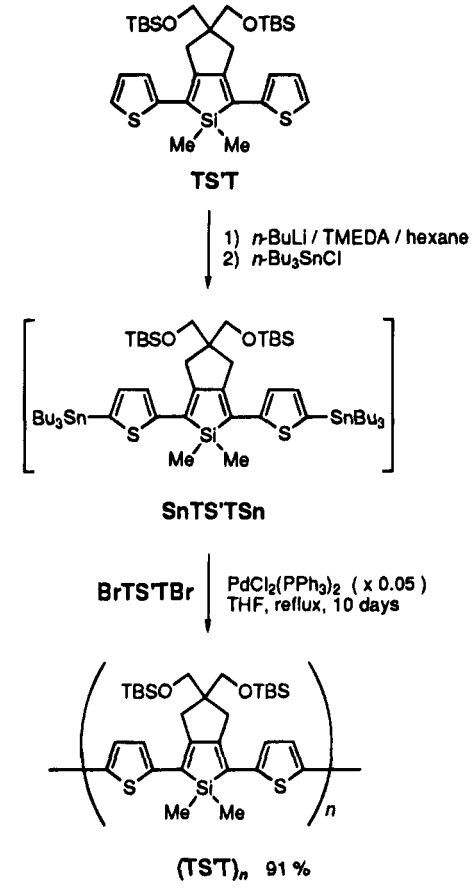


A three-rings system, TS′T, consisting of a thiophene–silole–thiophene skeleton, has been prepared as a monomer unit for the synthesis of silole–thiophene 1:2 and 1:3 copolymers, as shown in Scheme 1. Thus, TS′T was prepared in 77% yield by intramolecular cyclization of thiophene-containing 1,6-heptadiyne **2**[7] with 1,2-dihydrotetramethyldisilane (**3**) by use of a low-valent nickel complex as catalyst, which was generated in situ from bis(acetylacetonato)nickel(II), $Ni(acac)_2$ (5 mol %), triethylphosphine, PEt_3 (10 mol %), and diisobutylaluminum hydride, DIBAH (10 mol %).[8] In this reaction, the yield was strongly affected by the concentration of reaction mixtures: While the cyclization carried out in about 1 M concentration gave TS′T in 77% yield, a more dilute *ca.* 0.1 M condition lowered the yield to 40–50% and gave a considerable amount of hydrosilylated byproducts. The present cyclization is an intramolecular version of the intermolecular cyclization reported by Kumada and co-workers.[9] While the intermolecular cyclization of (alkyl)(aryl)acetylenes gives 2,5-dialkyl-3,4-diarylsiloles regioselectively, the intramolecular cyclization can reverse the regioselectivity to give fully conjugated 2,5-diarylsiloles.

Bromination of TS′T with 1.1 equiv of *N*-bromosuccinimide (NBS) in a DMF/THF mixed solvent gave a mixture of monobromide TS′TBr and dibromide BrTS′TBr (Scheme 1). Column chromatography isolation of the mixture afforded TS′TBr and BrTS′TBr in 47% and 16% yields, respectively. All of these three-ring compounds, TS′T, TS′TBr, and BrTS′TBr, are air-stable yellow crystals.

Synthesis of Silole–Thiophene 1:2 Copolymer: $(TS'T)_n$. The silole-thiophene 1:2 copolymer, $(TS'T)_n$, has been prepared by the Stille coupling,[10] as outlined in Scheme 2. Thus, a successive treatment of TS′T with *n*-BuLi/TMEDA and *n*-Bu_3SnCl afforded distannylated compound SnTS′TSn. Prolonged cross-coupling reaction of SnTS′TSn with BrTS′TBr catalyzed by 5 mol % of

Scheme 2



bis(triphenylphosphine)palladium chloride, $PdCl_2(PPh_3)_2$, in THF gave $(TS'T)_n$ as a red purple solid in 91% yield after reprecipitation from hexane. This sequence of reactions, from stannylation to coupling reaction, was performed in one pot.

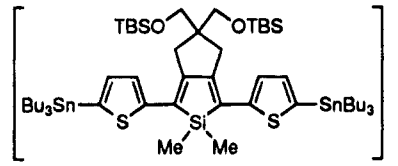
Synthesis of Silole–Thiophene 1:3 Copolymer: $(TTS'T)_n$. The silole-thiophene 1:3 copolymer, $(TTS'T)_n$, was prepared similarly by the palladium-catalyzed cross-coupling reaction of SnTS′TSn with 2,5-dibromothiophene in 84% yield as a gold red powder after reprecipitation from hexane (Scheme 3).

Synthesis of Silole–Thiophene 1:4 Copolymer: $(TTS'TT)_n$. We first attempted to prepare the silole-thiophene 1:4 copolymer by a similar route by the palladium-catalyzed cross-coupling reaction of SnTS′TSn and 2,5′-dibromo-2,2′-bithiophene, but the 1:4 copolymer could not be obtained as an analytically pure form. Therefore, the pure 1:4 copolymer was prepared by an alternative route outlined in Schemes 4 and 5.

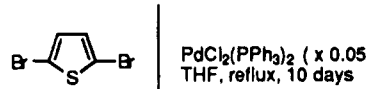
A new five-ring system, TTS′TT, was thus introduced as a monomer unit in place of TS′T. The TTS′TT was prepared in 66% yield as a red crystal by the nickel(0)-catalyzed intramolecular cyclization of bithienyl-terminated 1,6-heptadiyne **4** with dihydrodisilane **3**. TTS′TT was treated with *n*-BuLi/TMEDA in hexane followed by trapping with iodine to give a diiodo compound, ITTS′TTI, in 83% yield, as shown in Scheme 4. The palladium-catalyzed cross-coupling reaction of ITTS′TTI with SnTTS′TTSn, generated *in situ* from TTS′TT by successive treatment with *n*-BuLi/TMEDA and *n*-Bu_3SnCl, afforded the desired 1:4 copolymer, $(TTS'TT)_n$, in 95% yield as a golden red powder (Scheme 5).

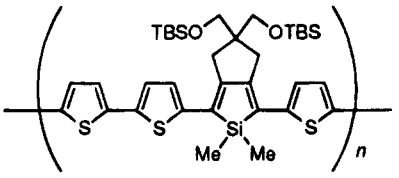
Solubility and Molecular Weight. All of the series of silole-thiophene copolymers, $(TS'T)_n$, $(TTS'T)_n$, and $(TTS'TT)_n$, are air-stable and soluble in common organic

Scheme 3



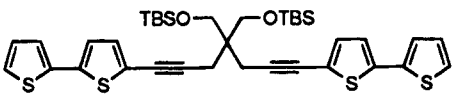
SnTS'TSn





$(TTS'T)_n$ 84 %

Scheme 4



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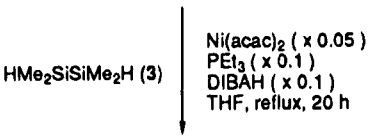
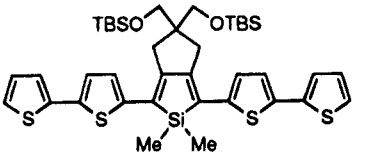
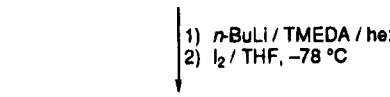
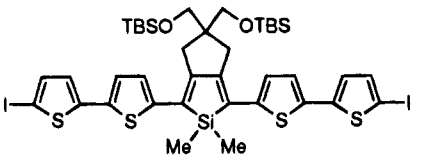




TTS'TT 66 %



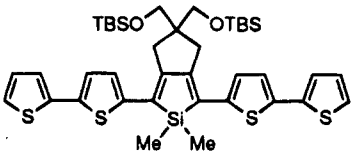


ITTS'TTI 83 %

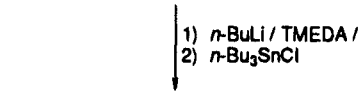
solvents such as THF, CH_2Cl_2, and $CHCl_3$. For example, the solubility of $(TTS'TT)_n$ in THF was 5.6 g/L. The solubility of the copolymers in THF decreases in the following sequence; first depending on the silole-thiophene ratio, $(TS'T)_n$ > $(TTS'T)_n$ > $(TTS'TT)_n$, and second depending on the nature of the substituents on silicon, $(TS'T)_n$ > $(TST)_n$. These sequences are apparently ascribed to the increased ratio of the aliphatic methyl substituents on the silicon atom of the silole ring.

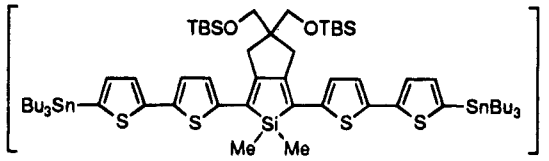
Molecular weight approximations, obtained by gel permeation chromatography (GPC) against a polystyrene standard,[11] are summarized in Table 1. While the degrees of polymerization (DP) are in the range of about

Scheme 5

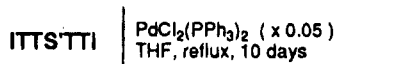


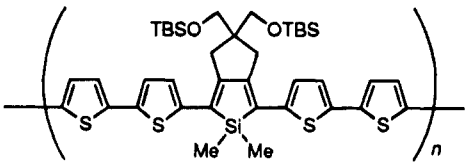
TTS'TT





SnTTS'TTSn





$(TTS'TT)_n$ 95 %

Table 1. Molecular Weights of Silole–Thiophene Copolymers[a]

polymer	M_w	M_n	M_w/M_n	DP(n)[b]	no. of rings[c]
$(TS'T)_n$	25,700	14,700	1.75	24	72
$(TTS'T)_n$	36,300	18,400	1.97	27	108
$(TTS'TT)_n$	69,400	31,700	2.19	41	205

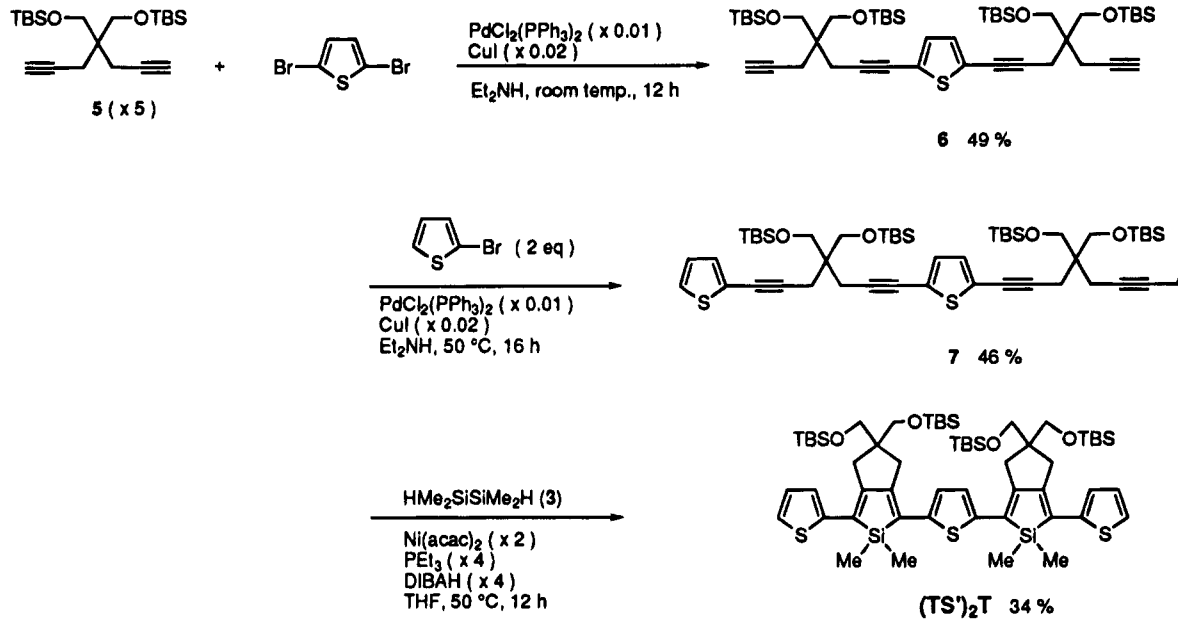
[a] Determined by GPC analysis *vs* polystyrene standard. [b] Average degrees of polymerization. [c] Number of rings contained in the main chain, estimated from the value of DP.

20–40, the total numbers of the rings in the main chain vary from *ca.* 70 to 200.

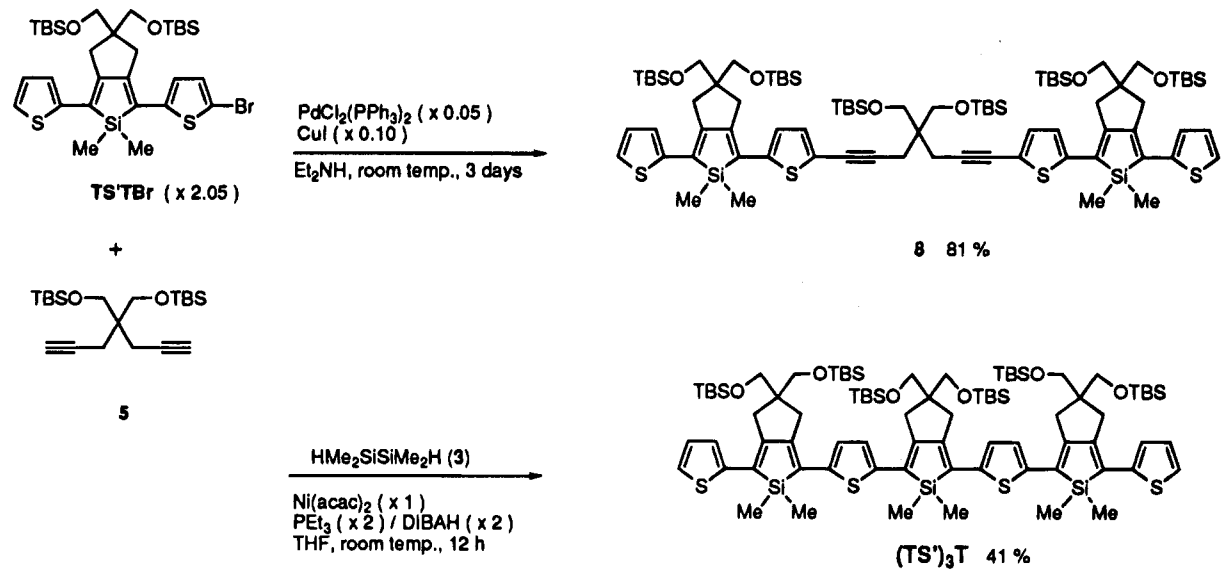
Synthesis of Silole–Thiophene Alternating 1:1 Cooligomers. A silole–thiophene 1:1 copolymer has been an attractive synthetic target compound in view of the anticipated novel properties. However, the 1:1 copolymer has been extremely hard to prepare by means of such a direct route as the homocoupling or cross-coupling reaction catalyzed by transition metal complexes, because of a great difficulty in the introduction of the requisite functional groups (such as halogen, lithium, and stannyl groups) into the 2,5-positions of the silole ring by conventional methods.[12–14] Therefore, we have now prepared silole-thiophene alternating cooligomers as models of the copolymer. The synthetic routes we adopted are the nickel(0)-promoted intramolecular cyclization of the thiophene–diyne cooligomers with disilane **3**, as shown in Schemes 6 and 7.

The precursor, thiophene–(1,6-heptadiyne) alternating cooligomer **7**, was prepared by the sequential Pd/Cu-catalyzed coupling reactions, as shown in Scheme 6:[15] the coupling reaction of 2,5-dibromothiophene with an excess amount of 4,4-bis[(*tert*-butyldimethylsiloxy)-methyl]-1,6-heptadiyne (**5**) (5 equiv) in the presence of $PdCl_2(PPh_3)_2$/CuI catalyst gave a 2,5-bis(1,6-heptadiyn-1-yl)thiophene derivative (**6**) in 49% yield, which was subsequently treated with 2 equiv of 2-bromothiophene

Scheme 6



Scheme 7



under similar conditions to afford compound **7** in 46% yield. Intramolecular cyclization of **7** with disilane **3** promoted by a stoichiometric amount of low-valent nickel complex, generated *in situ* from the $Ni(acac)_2$/PEt_3/DIBAH system, afforded a five-ring compound, $(TS')_2T$, in 34% yield. The use of a stoichiomeric amount of nickel complex instead of a catalytic amount is to promote the "double" intramolecular cyclization more efficiently.

Bis(TS'T-terminated)-1,6-heptadiyne **8** was also prepared by similar Pd/Cu-catalyzed coupling of the diyne **5** with 2 equiv of TS'TBr in 81% yield, as shown in Scheme 7. Intramolecular cyclization of **8** with disilane **3** promoted by a stoichiometric amount of nickel(0) complex gave a seven-ring compound, $(TS')_3T$, in 41% yield.

Both of the cooligomers, $(TS')_2T$ (red crystal) and $(TS')_3T$ (golden brown powder), are air-stable and soluble in THF, CH_2Cl_2, and $CHCl_3$ and slightly soluble in hydrocarbons such as hexane.

UV–Vis Absorption Spectra. The UV–visible absorption data in $CHCl_3$ of the cooligomers and the copolymers are summarized in Table 2, which contains some previous data for comparison.[1a] All of the silole–thiophene cooligomers and copolymers show much longer absorptions in the visible region compared with thiophene homooligomers and homopolymers.[1a] Significantly, there is a general tendency that the higher silole ratios (lower thiophene ratios) cause bathochromic shifts. Thus, in the oligomer series, the absorption maximum becomes longer from λ_{max} 505 nm for the S:T = 1:2 six-ring system $(TST)_2$ to λ_{max} 524 nm for the S':T = 2:3 five-ring system $(TS')_2T$, and further to λ_{max} 582 nm for the S':T = 3:4 seven-ring system $(TS')_3T$, which also exceeds λ_{max} 549 nm for the S:T = 1:2 nine-ring system $(TST)_3$. This tendency is also observed in the series of silole–thiophene copolymers. Thus, change of the silole–thiophene ratio from 1:4 to 1:2 leads to about a 70 nm bathochromic shift. The results may be ascribed to the lowering of the LUMO level in the π-systems accompanied by an increase in the silole content, as will be discussed in the final theoretical study section.

Table 2. UV–Visible Absorption Data for Silole–Thiophene Cooligomers and Copolymers[a]

compd	silole–thiophene ratio	λ_{max}/nm	(log ϵ)	ref
		cooligomer		
$(TS')_3T$	3:4 (7)[b]	544	(4.98)	this work
		582	(4.91)	
$(TS')_2T$	2:3 (5)[b]	490	(4.78)	this work
	524 (4.71)			
$(TST)_2$	1:2 (6)[b]	505	(4.86)	c
$(TST)_3$	1:2 (9)[b]	549	(4.96)	c
		copolymer		
$(TST)_n$	1:2	594	(4.52)[d]	c
		615	(4.51)[d]	
$(TS'T)_n$	1:2	576	(4.49)[d]	this work
		618	(4.44)[d]	
$(TTS'T)n$	1:3	546	(4.51)[d]	this work
$(TTS'TT)n$	1:4	549	(4.70)[d]	this work

[a] In chloroform. [b] Number of the rings contained in the main chain is in parentheses. [c] Tamao, K.; Yamaguchi, S.; Shiozaki, M.; Nakagawa, Y.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 5867. [d] Per monomer unit.

Table 3. Electrical Conductivities of Silole–Thiophene Cooligomers and Copolymers[a]

compds	silole–thiophene ratio	σ (S cm^{-1})[b]	ref
$(TS')_3T$	3:4	3.0×10^{-5}	this work
$(TS'T)_n$	1:2	1.3×10^{-1}	this work
$(TTS'T)_n$	1:3	1.0×10^{-1}	this work
$(TTS'TT)_n$	1:4	2.4	this work
$(TST)_n$	1:2	9.0×10^{-3}	c

[a] Determined on thin films of polymers cast on a glass substrate, by the use of the four-probe technique. [b] The values upon doping with iodine vapor. [c] Tamao, K.; Yamaguchi, S.; Shiozaki, M.; Nakagawa, Y.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 5867.

Electrical Conductivity. Electrical conductivities of four compounds, $(TS')_3T$, $(TS'T)_n$, $(TTS'T)_n$, and $(TTS'TT)_n$, with iodine doping, were measured by use of the four-probe technique. The results are summarized in Table 3. The alternating 1:1 cooligomer, $(TS')_3T$, exhibits a rather small conductivity (3×10^{-5} S cm^{-1}), probably partly due to its poor film-forming properties. Among the polymers, the conductivity increases in the order $(TS'T)_n \sim (TTS'T)_n < (TTS'TT)_n$. The highest conductivity 2.4 S cm^{-1} is still much lower than that (10^2–10^3 S cm^{-1}) of well-defined poly(3-alkylthiophene).[6] While it is difficult to make a strict discussion about a relationship between these conductivities and the silole–thiophene ratios because of the different chain lengths of the polymers, these results imply that the decrease in the silole content tends to afford higher conductivities. This tendency may be explained as follows: The bulky (*tert*-butyldimethylsiloxy)methyl groups in the silole unit are oriented out of the π-conjugated polymer plane and hence hinder the interaction between polymer chains (plains), which is one of the key factors for high conductivity.[16]

***Ab Initio* Calculations for Electronic Structures of Silole–Thiophene Cooligomers.** To elucidate the electronic structures of silole–thiophene mixed systems in more detail,[17] we performed theoretical calculations for the one-ring systems, thiophene (T) and parent silole (S″), and three-ring systems, terthiophene (TTT) and TS″T. *Ab initio* molecular orbital calculations for S″ and T, performed at the RHF/6-31G* level of theory, demonstrate the following two significant features:[18] (1) Silole has a considerably lower LUMO compared with thiophene, and (2) in the LUMO of silole there is a lobe on silicon in-phase with lobes on the adjacent ring carbons (Figure 1). It should be noted that silole has a slightly higher HOMO than thiophene as well.

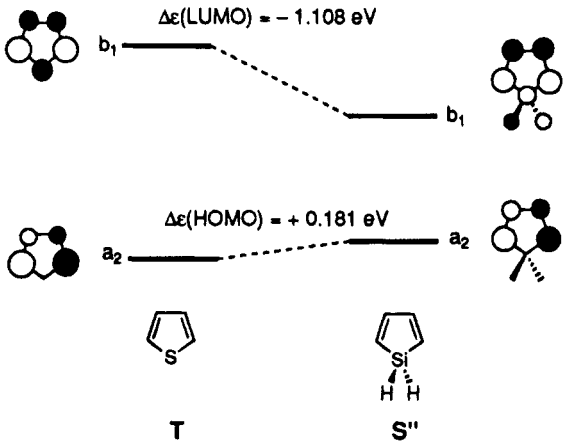


Figure 1. Relative energy levels of HOMO and LUMO for T and S″, based on *ab initio* calculations at the RHF/6-31G* level of theory.

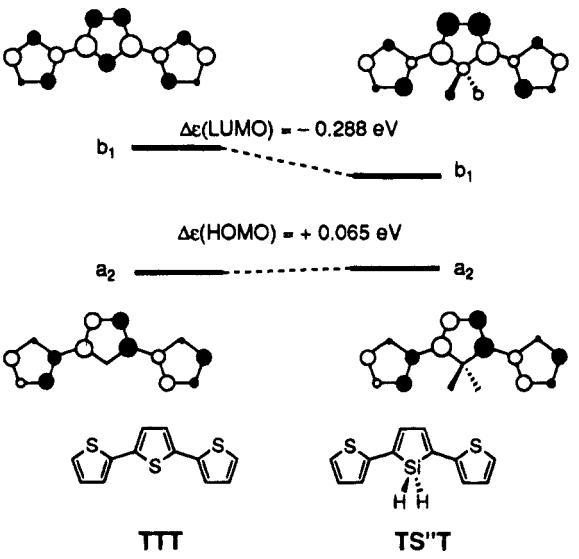


Figure 2. Relative energy levels of HOMO and LUMO for TTT and TS″T, based on *ab initio* calculations at the RHF/6-31G* level of theory.

Similar calculations for the three-ring systems, TS″T and TTT, were also performed at the RHF/6-31G* level of theory, as shown in Figure 2. The HOMO of TS″T lies in almost the same level as that of TTT. A significant difference in the electronic structures between TS″T and TTT is observed in those LUMO levels. Thus, the silole-containing three-ring system, TS″T, has about a 0.3 eV lower LUMO than TTT, evidently ascribed to the contributions of the lower LUMO of the silole ring.

As mentioned in the Introduction, we primarily anticipated that silole acted as the electron-accepting part and thiophene as the electron-donating part in the copolymers, according to the traditional classification of heteroaromatic compounds, in which thiophene falls into a class of π-electron excessive rings.[19] The *ab initio* calculation for S″ and T, however, suggests that actually silole has stronger electron-donating properties. Therefore, it seems reasonable to say that the unique electronic structures of the present π-systems do not result from a combination of electron-donating and electron-accepting rings, but are mainly caused by the introduction of the silole ring that carries the unusually low-

Table 4. Electrochemical Data for TS'T and TTT[a]

compd	E_{pa1}, E_{pa2} (V)[b]	E_{pc1}, E_{pc2}, E_{pc3} (V)[b]
TS'T	0.57	−2.36, −2.61
TTT	0.80, 0.88	−2.53, −2.72, −2.95

[a] Determined by cyclic voltammetry. [b] All potentials, *vs* Ag/Ag^+ in acetonitrile, are corrected with reference to ferrocene ($E_{1/2}$ +0.083 V) used as an internal standard.

lying LUMO and rather high-lying HOMO levels. These results are well consistent with the tendency that the higher silole compositions cause red shifts in the UV–vis absorption spectra.

The accuracy of the present calculation results are supported experimentally. The electrochemical data for TTT and TS'T, determined by cyclic voltammetry, are summarized in Table 4. TS'T has the first reduction potential (E_{pc1}) at about 0.17 V anodic position compared with that of terthiophene. In contrast, the oxidation potential (E_{pa}) of TS'T is 0.23 V lower than the first oxidation potential (E_{pa1}) of TTT.

Summary and Conclusion

A series of silole–thiophene cooligomers and copolymers have been synthesized by nickel-promoted intramolecular cyclizations and palladium-catalyzed cross-coupling reactions. In the UV–vis absorption spectra, silole–thiophene mixed systems show red shifts with higher silole compositions. In contrast, the electrical conductivities of the copolymers tend to become higher with lower contents of siloles, attached by the bulky side chains oriented out of the π-conjugated polymer plane. Thus, the present results strongly suggest that the introduction of silole rings which possess smaller out-of-plane substituents, especially into the 1:1 alternating copolymers, would be most promising for development of novel π-electronic materials of some applicabilities. Further study in this line is now in progress in our laboratory.

Ab initio calculation studies have demonstrated the unusual electronic structures of the silole ring which has relatively higher HOMO and much lower LUMO levels compared with thiophene. One may say that silole is a prominent π-conjugated ring as an electron-accepting component in the combined π-conjugated systems with more electron-donating rings such as pyrroles. This project is also under investigation in our laboratory.

Experimental Section and Calculations

General Information. ^1H and ^{13}C NMR spectra were measured with a Varian VXR-200 (200 MHz for ^1H and 50 MHz for ^{13}C) spectrometer in $CDCl_3$. Chemical shifts are reported in δ, ppm. UV–vis spectra were obtained on a Hitachi U-3410. Cyclic voltammograms were obtained on a BSA CV-50W. Thin layer chromatography (TLC) was performed on plates coated with a 0.25 mm thickness of silica gel 60F-254 (Merck). Column chromatography was performed by using Kieselgel 60 (70–230 mesh) (Merck).

Materials. THF was distilled from sodium/benzophenone. Other all solvents were dried over appropriate desiccants and distilled under nitrogen. Bis(acetylacetonato)nickel(II) is commercially available and dried in vacuo (100 °C, 0.5 mmHg, 10 h) before use. Bis(triphenylphosphine)palladium(II) chloride was prepared as reported in the literature.[20] Triethylphosphine was commercially available. Diisobutylaluminum hydride was purchased from Aldrich Co. Ltd. as a 1 M hexane solution. 4,4-Bis[(*tert*-butyldimethylsiloxy)methyl]-1,6-heptadiyne (**5**) and 4,4-bis[(*tert*-butyldimetylsiloxy)methyl]-1,7-bis(2-thienyl)-1,6-heptadiyne (**2**) were prepared as described in our previous report.[1a] 1,2-Dihydro-1,1,2,2-tetramethyldisilane (**3**) was prepared by reduction of 1,2-dichloro-1,1,2,2-tetramethyldisilane[21] with lithium aluminum hydride. 5-Bromo-2,2'-bithiophene was prepared from 2,2'-bithiophene by use of NBS in a 1/1 $CHCl_3$/AcOH mixed solvent.[22] All reactions were carried out under a nitrogen atmosphere.

General Procedure for Nickel(0)-Catalyzed Intramolecular Cyclization of Diyne with Hydrodisilane: Preparation of TS'T. A nickel catalyst solution was prepared as follows: To a solution of $Ni(acac)_2$ (64 mg, 0.25 mmol) in THF (2 mL) were added successively PEt_3 (74 μL, 0.5 mmol) and DIBAH (1 M solution in hexane; 0.5 mL, 0.5 mmol) at room temperature, and the mixture was stirred for 0.5 h. To a mixture of diyne **2** (2.72 g, 5mmol) and dihydrodisilane **3** (0.59 g, 5 mmol) in dry THF (3 mL) was added dropwise the nickel catalyst solution at room temperature. The mixture was refluxed with stirring for 17 h. After confirmation of the disappearance of **2** by TLC, the solvent was evaporated under reduced pressure. The residue was subjected to column chromatography on silica gel (hexane, $R_f = 0.39$) to give 2.31 g (3.83 mmol) of TS'T (bright yellow crystal) in 77% yield: mp 148–149 °C. ^1H NMR ($CDCl_3$): δ 0.01 (s, 12H), 0.51 (s, 6H), 0.88 (s, 18H), 2.55 (s, 4H), 3.53 (s, 4H), 6.93 (dd, 2H, J = 1.0 and 3.6 Hz), 7.03 (dd, 2H, J = 3.6 and 5.2 Hz), 7.24 (dd, 2H, J = 1.0 and 5.2 Hz). ^{13}C NMR ($CDCl_3$): δ −5.47, −1.91, 18.32, 25.94, 35.90, 52.44, 65.57, 124.33, 124.41, 125.76, 127.26, 143.82, 155.97. Anal. Calcd for $C_{31}H_{50}O_2Si_3S_2$: C, 61.74; H, 8.36. Found: C, 61.52; H, 8.43.

TS'TBr and BrTS'TBr. To a solution of TS'T (200 mg, 0.337 mmol) in THF (4 mL) was added dropwise a DMF (2 mL) solution of NBS (64 mg, 0.36 mmol) at room temperature. The mixture was stirred for 15 min: Prolonged reaction period caused a desilylation of the *tert*-butyldimethylsilyl groups. The mixture was diluted with water (50 mL) and extracted with hexane (20 mL x 3). The combined extract was washed with water (50 mL x 3) and brine (50 mL) and then dried over Na_2SO_4. After filtration and evaporation of solvents, the residue was passed through a short silica gel column (hexane/CH_2Cl_2 = 20/1) and subjected to MPLC on silica gel (hexane/CH_2Cl_2 = 20/1) to give both TS'TBr ($R_f = 0.26$; 108 mg, 0.159 mmol, 47% yield) and BrTS'TBr ($R_f = 0.34$; 41 mg, 0.054 mmol, 16% yield) in pure form.

TS'TBr: yellow crystal; mp 125 °C. ^1H NMR ($CDCl_3$): δ 0.02 (s, 12H), 0.49 (s, 6H), 0.88 (s, 18H), 2.48 (s, 2H), 2.56 (s, 2H), 3.53 (s, 4H), 6.65 (d, 1H, J = 3.8 Hz), 6.93 (br d, 1H, J = 2.6 Hz), 6.97 (d, 1H, J = 3.8 Hz), 7.04 (dd, 1H, J = 3.8 and 5.4 Hz), 7.26 (br d, 1H, J = 5.6 Hz). ^{13}C NMR ($CDCl_3$): δ −5.48, −1.95, 18.32, 25.93, 35.85, 52.53, 65.61, 110.78, 124.30, 124.59, 125.36, 126.16, 127.30, 130.06, 143.58, 145.58, 155.75, 156.60. Anal. Calcd for $C_{31}H_{49}O_2Si_3S_2Br$: C, 54.59; H, 7.24. Found: C, 54.72; H, 7.32.

BrTS'TBr: yellow crystal; mp 127–128 °C. ^1H NMR ($CDCl_3$): δ 0.01 (s, 12H), 0.47 (s, 6H), 0.88 (s, 18H), 2.47 (s, 4H), 3.51 (s, 4H), 6.64 (d, 2H, J = 3.8 Hz), 6.96 (d, 2H, J = 3.8 Hz). ^{13}C NMR ($CDCl_3$): δ −5.49, −1.99, 18.31, 25.91, 35.81, 52.62, 65.66, 111.07, 124.50, 125.71, 130.10, 145.34, 156.39. Anal. Calcd for $C_{31}H_{48}O_2Si_3S_2Br_2$: C, 48.93; H, 6.36. Found: C, 49.10; H, 6.50.

General Procedure for One-Pot Synthesis of Silole–Thiophene Copolymers: Preparation of $(TS'T)_n$. To a solution of TS'T (33.2 mg, 55 μmol) in dry hexane (2 mL) were added successively TMEDA (33 μL, 220 μmol) and *n*-BuLi (1.57 M hexane solution; 140 μL, 220 μmol) at room temperature. The mixture was stirred at room temperature for 1 h. Tri-*n*-butyltin chloride (65 μL, 240 μmol) was added to the mixture at room temperature followed by stirring for 1 h. After removal of the solvent under reduced pressure, $PdCl_2(PPh_3)_2$ (2 mg, 2.8 mmol) and a solution of BrTS'TBr (41.8 mg, 55 μmol) in THF (5 mL) were successively added to the residue. The mixture was refluxed with stirring for 10 days. After evaporation of solvents, the residue was dissolved in chloroform (50 mL). The ink-blue chloroform solution was washed with an aqueous solution of potassium cyanide (ca. 10 mM; 40 mL x 2) and water (50 mL x 1), and dried over Na_2SO_4. After filtration and evaporation of the solvent, the residue was dissolved in a small amount of chloroform. The chloroform solution was added to ethanol to cause precipitation of

polymer, which was filtered out and washed with ethanol. The polymer was obtained as a metallic red violet solid (60.4 mg; 91% yield): ^{1}H NMR ($CDCl_3$): δ 0.04 (s, 12H), 0.54 (s, 6H), 0.92 (s, 18H), 2.60 (br s, 4H), 3.58 (br s, 4H), 6.58 (br d, 2H, J = 3.0 Hz), 7.10 (br d, 2H, J = 3.0 Hz). ^{13}C NMR ($CDCl_3$): δ −5.43, −1.76, 18.36, 25.98, 36.21, 52.64, 65.68, 123.57, 125.72, 126.21, 136.67, 142.87, 156.32. Anal. Calcd for $(C_{31}H_{48}O_2Si_3S_2)_n$: C, 61.94; H, 8.05. Found: C, 56.29; H, 8.06.

(TTS′T)$_n$. Polymer (TTS′T)$_n$ (gold red powder) was prepared in 84% yield in essentially the same manner described for (TS′T)$_n$ by use of 2,5-dibromothiophene in place of BrTS′TBr: ^{1}H NMR ($CDCl_3$): δ 0.04 (s, 12H), 0.54 (s, 6H), 0.91 (s, 18H), 2.60 (br s, 4H). 3.57 (br s, 4H), 6.78−6.88 (m, 4H), 6.94−7.16 (m, 4H). ^{13}C NMR ($CDCl_3$): δ −5.43, −1.82, 18.36, 25.96, 36.11, 52.64, 65.69, 123.72, 123.91, 125.65, 126.19, 135.94, 136.33, 143.09, 156.55. Anal. Calcd for $(C_{35}H_{50}O_2Si_3S_3)_n$: C, 61.53; H, 7.38. Found: C, 58.64; H, 7.24.

1,7-Bis(2,2′-bithien-5-yl)]-4,4-bis[(*tert*-butyldimethylsiloxy)methyl]-1,6-heptadiyne (4). To a mixture of 5-bromo-2,2′-bithiophene (1.62 g, 6.6 mmol), $PdCl_2(PPh_3)_2$ (19 mg, 27.5 μmol), and CuI (11 mg, 55 μmol) in diethylamine (1 mL) was added a solution of diyne **5** (1.05 g, 2.75 mmol) in 4 mL of diethylamine. The reaction mixture was heated at 50 °C with stirring for 11 h. After confirmation of the disappearance of starting diyne by TLC, the mixture was filtered and evaporated. The residue was subjected to column chromatography on silica gel (hexane, R_f = 0.09) to give 1.85 g (2.61 mmol, 95% yield) of diyne **4** as a viscous oil. ^{1}H NMR ($CDCl_3$): δ 0.08 (s, 12H), 0.91 (s, 18H), 2.56 (s, 4H), 3.61 (s, 4H), 6.96−7.03 (m, 6H), 7.14 (dd, 2H, J = 1.2 and 3.5 Hz), 7.20 (dd, 2H, J = 1.2 and 5.1 Hz). ^{13}C NMR ($CDCl_3$): δ −5.48, 18.33, 22.66, 25.92, 44.72, 63.66, 75.58, 92.40, 122.86, 123.25, 123.95, 124.67, 127.85, 131.87, 136.91, 137.54.

TTS′TT. TTS′TT was prepared in 66% yield according to the procedure described for TS′T using diyne **4** in place of diyne **2**. Purification by column chromatography on silica gel (hexane/EtOAc = 100/1, R_f = 0.17) afforded 131 mg (0.13 mmol, 46% yield) of TTS′TT as a red crystal: mp 150 °C. ^{1}H NMR ($CDCl_3$): δ 0.03 (s, 12H), 0.53 (s, 6H), 0.90 (s, 18H), 2.59 (s, 4H), 3.56 (s, 4H), 6.83 (d, 2H, J = 3.9 Hz), 7.01 (dd, 2H, J = 3.7 and 5.0 Hz), 7.11 (d, 2H, J = 3.9 Hz), 7.15 (dd, 2H, J = 1.1 and 3.7 Hz), 7.19 (dd, 2H, J = 1.1 and 5.0 Hz). ^{13}C NMR ($CDCl_3$): δ −5.45, −1.83, 18.34, 25.94, 36.07, 52.59, 65.60, 123.14, 124.05, 125.43, 126.07, 127.86, 136.09, 137.87, 142.98, 156.33. Anal. Calcd for $C_{39}H_{54}O_2Si_3S_4$: C, 61.04; H, 7.09. Found: C, 61.36; H, 7.34.

ITTS′TTI. To a solution of TTS′TT (46 mg, 60 μmol) in hexane (5 mL) was added successively TMEDA (22 μL, 144 μmol) and n-BuLi (1.59M in hexane; 90 μL, 144 μmol). The mixture was stirred at room temperature for 1 h and cooled to −78 °C. A solution of I_2 (37 mg, 144 μmol) in THF (1 mL) was added to the mixture at −78 °C. The resulting mixture was gradually warmed to room temperature with stirring over 1 h. A saturated Na_2SO_3 aqueous solution was added to the mixture and the mixture was extracted with ether. The combined organic layer was washed with brine and dried over Na_2SO_4. After filtration and removal of the solvents under reduced pressure, the residue was subjected to column chromatography on silica gel (hexane/EtOAc = 25/1, R_f = 0.36) to give 51 mg (50 μmol, 83% yield) of ITTS′TTI as a red crystal: mp 142−144 °C. ^{1}H NMR ($CDCl_3$): δ 0.03 (s, 12H), 0.52 (s, 6H), 0.89 (s, 18H), 2.57 (s, 4H), 3.55 (s, 4H), 6.82 (d, 4H, J = 3.8 Hz), 7.04 (d, 2H, J = 3.8 Hz), 7.14 (d, 2H, J = 3.8 Hz). ^{13}C NMR ($CDCl_3$): δ −5.45, −1.88, 18.34, 25.93, 36.06, 52.63, 65.61, 124.43, 124.50, 125.51, 126.15, 134.88, 137.72, 143.41, 143.72, 156.77. FABMS: m/z 1019 (M^+).

(TTS′TT)$_n$. (TTS′TT)$_n$ was prepared in essentially the same manner described for (TS′T)$_n$ by use of ITTS′TTI (181.7 mg, 0.178 mmol) and SnTTS′TTSn, generated *in situ* from TTS′TT (136.6 mg, 0.178 mmol). Reprecipitation from hexane afforded (TTS′TT)$_n$ (260 mg, 95% yield) as a golden red purple powder. ^{1}H NMR ($CDCl_3$): δ 0.04 (s, 12H), 0.54 (s, 6H), 0.91 (s, 18H), 2.60 (br s, 4H), 3.57 (br s, 4H), 6.81−6.88 (m, 2H), 7.01−7.15 (m, 6H). ^{13}C NMR ($CDCl_3$): δ −5.42, −1.81, 18.37, 25.98, 36.14, 52.65, 65.64, 123.85, 124.09, 124.28, 125.66, 126.22, 135.64, 135.82, 136.67, 143.24, 156.65. Anal. Calcd for $(C_{39}H_{52}O_2Si_3S_4)_n$: C, 61.20; H, 6.85. Found: C, 59.40; H, 6.98.

Bis(diyne) 6. Compound **6** was prepared in essentially the same manner described for preparation of diyne **4** by use of diyne **5** (1.9 g, 5 mmol) and 2,5-dibromothiophene (242 mg, 1 mmol). Purification by MPLC on silica gel (hexane, R_f = 0.18) gave 411 mg (0.49 mmol, 49% yield) of **6** in pure form as a viscous oil. ^{1}H NMR ($CDCl_3$): δ 0.05 (s, 24H), 0.89 (s, 36H), 1.95 (t, 2H, J = 2.6 Hz), 2.29 (d, 4H, J = 2.6 Hz), 2.49 (s, 4H), 3.55 (s, 8H), 6.90 (s, 2H). ^{13}C NMR ($CDCl_3$): δ −5.57, 18.27, 21.17, 22.29, 25.86, 43.99, 63.38, 70.21, 75.27, 81.13, 91.73, 124.22, 130.66. Anal. Calcd for $C_{46}H_{80}O_4Si_4S$: C, 65.65; H, 9.58. Found: C, 65.44; H, 9.70.

Bis(diyne) 7. Bis(diyne) **7** was prepared in essentially the same manner described for diyne **4** by use of **6** (238 mg, 0.283 mmol) and 2-bromothiophene (111 mg, 0.68 mmol). Purification by MPLC on silica gel (hexane/EtOAc = 30/1, R_f = 0.32) affoded 131 mg (0.13 mmol, 46% yield) of **7** as a viscous oil. ^{1}H NMR ($CDCl_3$): δ 0.08 (s, 24H), 0.91 (s, 36H), 2.54 (s, 8H), 3.61 (s, 8H), 6.92 (s, 2H), 6.93 (dd, 2H, J = 3.7 and 5.2 Hz), 7.11 (dd, 2H, J = 1.2 and 3.7 Hz), 7.17 (dd, 2H, J = 1.2 and 5.2 Hz). ^{13}C NMR ($CDCl_3$): δ −5.52, 18.31, 22.56, 25.90, 44.67, 63.69, 75.39, 75.61, 91.18, 91.82, 124.15, 124.29, 125.94, 126.72, 130.69, 130.99.

(TS′)$_2$T. (TS′)$_2$T was prepared according to the procedure described for TS′T using bis(diyne) **7** (95 mg; 0.095 mmol), dihydrodisilane **3** (33 mg, 0.28 mmol), $Ni(acac)_2$ (49 mg, 0.19 mmol), PEt_3 (56 μL, 0.38 mmol), and DIBAH (1 M in hexane; 0.38 mL, 0.38 mmol). Purification by MPLC on silica gel (hexane/EtOAc = 40/1, R_f = 0.24) gave a pure (TS′)$_2$T (36 mg, 32 mmol) in 34% yield as a red crystal: mp 211−213 °C. ^{1}H NMR ($CDCl_3$): δ 0.03 (s, 24H), 0.52 (s, 12H), 0.90 (s, 36H), 2.56 (s, 4H), 2.59 (s, 4H), 3.55 (s, 8H), 6.89 (s, 2H), 6.94 (br d, 2H, J = 3.4 Hz), 7.04 (dd, 2H, J = 3.6 and 5.1 Hz), 7.25 (br d, 2H, J = 4.5 Hz). ^{13}C NMR ($CDCl_3$): δ −5.45, −5.41, −1.78, 18.32, 25.98, 36.09, 52.44, 65.56, 124.32, 125.52, 125.71, 126.31, 127.28, 143.20, 143.94, 155.41, 156.36. Anal. Calcd for $C_{58}H_{96}O_4Si_6S_3$: C, 62.08; H, 8.62. Found: C, 62.21; H, 8.82.

Diyne 8. Diyne **8** was prepared in essentially the same manner described for **4** by use of diyne **5** (65 mg, 0.17 mmol) and TS′TBr (237mg, 0.35 mmol). Purification by MPLC on silica gel (hexane/EtOAc = 40/1, R_f = 0.26) afforded diyne **8** (218 mg, 0.138 mmol) in 81% yield as a yellow viscous oil: ^{1}H NMR ($CDCl_3$): δ 0.01 (s, 24H), 0.08 (s, 12H), 0.49 (s, 12H), 0.87 (s, 36H), 0.91 (s, 18H), 2.53 (s, 4H), 2.55 (s, 4H), 2.57 (s, 4H), 3.52 (s, 8H), 3.62 (s, 4H), 6.75 (d, 2H, J = 3.8 Hz), 6.93 (br d, 2H, J = 3.0 Hz), 7.03 (dd, 2H, J = 3.6 and 5.2 Hz), 7.03 (d, 4H, J = 3.8 H), 7.25 (br d, 2H, J = 5.0 Hz).

(TS′)$_3$T. (TS′)$_3$T was prepared in essentially the same manner described for TS′T using diyne **8** (218 mg, 0.138 mmol), disilane **3** (33 mg, 0.276 mmol), $Ni(acac)_2$ (35 mg, 0.138 mmol), PEt_3 (41 μL, 0.276 mmol), and DIBAH (1 M in hexane; 0.28 mL, 0.28 mmol). Purification by MPLC on silica gel (hexane/CH_2Cl_2 = 5/1, R_f = 0.41) gave 92 mg of (TS′)$_3$T (56 μmol, 41% yield) as a red-purple solid: mp 255 °C. ^{1}H NMR ($CDCl_3$): δ 0.03 (s, 24H), 0.04 (s, 12H), 0.52 (s, 18H), 0.89 (s, 36H), 0.91 (s, 18H), 2.56 (br s, 12H), 3.55 (br s, 12H), 6.88 (br s, 4H), 6.93 (br d, 2H, J = 3.4 Hz), 7.04 (dd, 2H, J = 3.6 and 5.2 Hz), 7.24 (br d, 2H, J = 5.0 Hz). ^{13}C NMR ($CDCl_3$): δ −5.42, −1.81, −1.68, 18.30, 25.97, 36.10, 36.25, 52.43, 65.56, 124.28, 125.41, 125.47, 125.58, 126.27, 126.31, 127.29, 143.35, 143.97, 155.84. Anal. Calcd for $C_{85}H_{142}O_6Si_9S_4$: C, 62.21; H, 8.72. Found: C, 62.24; H, 8.85.

Calculations. *Ab initio* calculations on S″, T, TS″T, and TTT were carried out with the GAUSSIAN 92 program using the restricted Hartree−Fock (RHF) approximation.[23] Geometry optimizations for S″ and T were perfomed with the 6-31G* basis set under constraints of the C_{2v} symmetry point groups. Geometry optimizations for TS″T and TTT were also performed with 6-31G* basis set under constraints of the C_{2v} symmetry point groups and *anti*-conformations concerning the ring orientations. The optimized geometries and total energy for these compounds are shown in supporting information.

Cyclic Voltammetry Measurements. The measurements were carried out under the following conditions: sample, 0.1 mM; solvent system, Bu_4NClO_4 (0.1 M) in acetonitrile; a glassy-

carbon working electrode, a platinum wire counter electrode, and an Ag/0.01 M $AgNO_3$ (acetonitrile) reference electrode; scan rate, 100 mV s^{-1}. The observed potentials were corrected with reference to ferrocene ($E_{1/2}$ +0.083 V) added as an internal standard after each measurement. All redox processes observed for TTT and TS'T were irreversible.

Acknowledgment. We greatly acknowledge the Grant-in-Aids (Nos. 04555203, 06451377, and 07555280) from the Ministry of Education, Science and Culture of Japan and partial financial support by Nagase Science and Technology Foundation and Ciba-Geigy Foundation (Japan) for the Promotion of Science. Computation time was provided by the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University.

Supporting Information Available: Tables of Cartesian Coordinates for Optimized geometries and total SCF energies (3 pages). Ordering information is given on any current masthead page.

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MA950617E