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General Synthesis of Extended Fused Oligothiophenes Consisting of an Even Number of Thiophene Rings

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Abstract: The intramolecular double cyclization of bis(3-bromo-2-thienyl)acetylenes though a lithium–halogen exchange reaction with *t*BuLi followed by treatment with elemental sulfur produces two thiophene-fused thieno[3,2-*c*](1,2-dithiin)s. The subsequent dechalcogenation from the 1,2-dithiins with copper nanopowder affords tetrathienoacenes. On the basis of this two-step procedure, a series of trialkylsilyl-terminated, fused oligothiophenes, including hexathienoacene (a six thiophene-fused system) and octathienoacene (an eight thiophene-fused system), were synthesized. In the UV/Vis absorption and fluorescence spectra of the fused oligothiophenes, the absorption and emission maxima shift to longer wavelengths, as the π-conjugation length increases. Their maximum wavenumbers have linear relationships with the reciprocal number of thiophene rings consisting of the π-conjugated frameworks. In the cyclic voltammograms, all the compounds show reversible oxidation waves, the first oxidation potential of which shifts to less positive as the conjugation length increases. Among them, the octathienoacene also shows a reversible second oxidation process. Indeed, its chemical oxidation with an excess amount of $NO^+SbF_6^-$ produces the dication as a golden crystal. The crystal structures of the neutral octathienoacene and its dication were determined by X-ray crystallography. While in the neutral state, the octathienoacene has a benzenoid structure with a large bond alternation of about 0.04 Å, its dication has a quinoid structure in which two cationic charges are mainly localized on the terminal rings.

Keywords: alkynes · cyclization · fused-ring systems · oligothiophenes · organic transistors

Introduction

Linearly fused π-conjugated systems are an important class of materials in the area of organic electronics.[1–4] Not only are their rigid and flat π-conjugated frameworks without conformational disorder, but also their unique electronic structures make them intriguing candidates for a broad spectrum of electronic and optoelectronic applications, including organic field-effect transistors (OFETs),[5–7] light-emitting diodes,[8] and solid-state lasers.[9,10] Fused oligothiophenes are a representative example, which can be recognized as the thiophene analogues of acenes. When compared with acenes such as pentacene, the fused oligothiophenes have two characteristic features concerning electronic and solid-state structures. First, while the acenes have a large quinoid character and thus narrow HOMO–LUMO gaps, the fused oligothiophenes have wide HOMO–LUMO gaps, since each thiophene ring retains the aromatic character. Second, the fused oligothiophenes favors a face-to-face π-stacked structure in the crystal packing, in sharp contrast to the herringbone structures generally observed for unsubstituted acenes.[11] While in the crystal structures of the acenes, the intermolecular edge-to-face interaction between the peripheral C−H bonds of one molecule with the π planes of neighboring molecules may be dominant, in the fused oligothiophenes, the nonbonding sulfur–sulfur interaction may play an important role. These features make them intriguing as environmentally stable and transparent carrier transporting materials for OFETs.[12]

From a synthetic viewpoint, however, only limited attention has been paid to the chemistry of the fused oligothiophenes to date.[11–20] Schroth and co-workers synthesized dibenzo-fused dithieno[3,2-*b*:2′,3′-*d*]thiophene **1** by dechalcogenation of the corresponding 1,2-dithiin precursor.[13] Kobayashi and co-workers prepared pentathienoacene **2** (five thiophene-fused system)[14] and investigated its electronic

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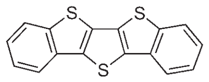
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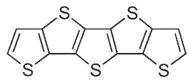
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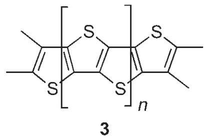

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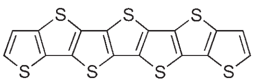
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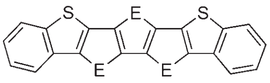
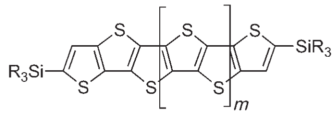

5 (E = S, Se)

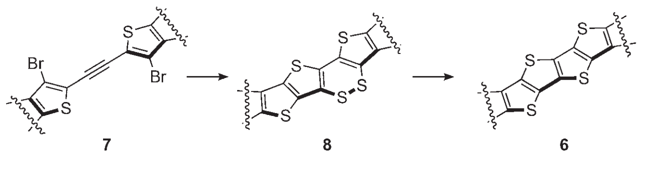


6a ($m = 0$)
6b ($m = 1$)
6c ($m = 2$)

structure.[15] Oyaizu and Tsuchida reported the synthesis of fused polythiophenes **3** based on the polymer-to-polymer transformation by means of an electrophilic annulation reaction.[16] Matzger and co-workers also reported the synthesis of heptathienoacenes **4** (seven thiophene-fused system) through the coupling of two dithieno[3,2-*b*:2′3′-*d*]thiophene moieties with a sulfur atom, followed by oxidative annulation,[11] and recently investigated its properties based on the Raman and UV-Vis-NIR studies.[17] We have also presented a synthetic route to the fused heteroacenes **5** consisting of thiophene or selenophene rings on the basis of the intramolecular triple cyclization from bis(*o*-haloaryl)diacetylenes (vide infra).[18,19] Whereas these several routes to the fused oligothiophenes and related compounds have already been developed, the development of more general and facile synthetic methods not only for longer oligomers, but also for a wide range of derivatives would be required for further progress in this chemistry. In this article, we disclose a general synthetic route to a series of fused oligothiophenes **6** that consist of an even number of thiophene rings. The fundamental photophysical and electrochemical properties of the produced fused oligothiophenes as well as the chemical oxidation are also described.

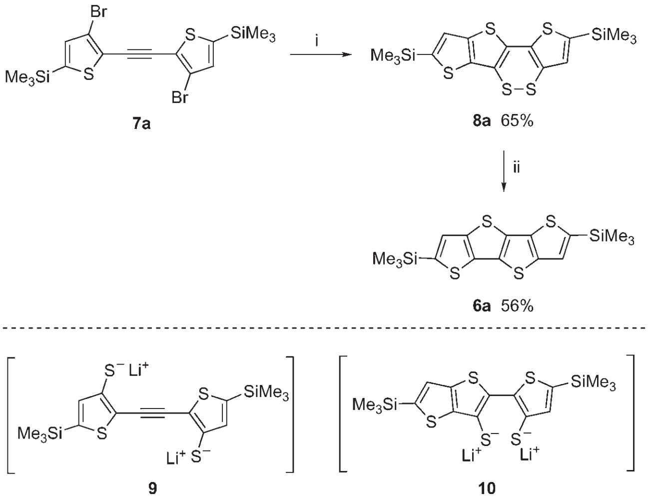
Results and Discussion

General synthesis of fused oligothiophenes: The outline of our synthesis is shown in Scheme 1, which includes two-step reactions. The first step is the intramolecular double cyclization of bis(3-halothienyl)acetylenes **7** to two thiophene-fused thieno[3,2-*c*](1,2-dithiin)s **8**. The second step of the reactions is the dechalcogenation reaction from the 1,2-dithiins to the target fused oligothiophenes **6**. The latter transformation was originally reported by Schroth and co-workers.[13]



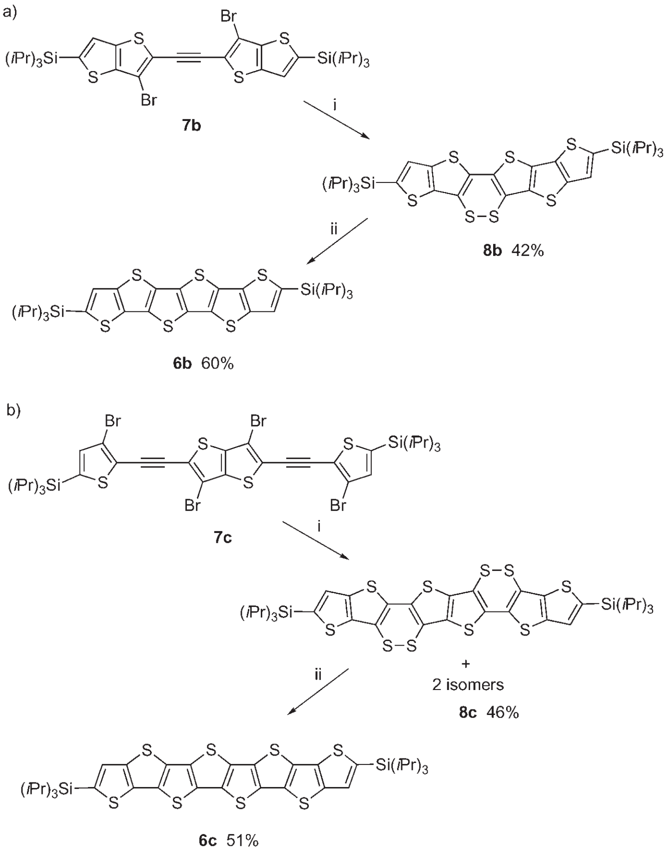
Scheme 1. Two-step synthesis of fused oligothiophenes from bis(3-halothienyl)acetylenes.

A typical procedure for the preparation of the tetrathienoacene **6a** is as follows (Scheme 2). Thus, the lithium–halogen exchange reaction of the dithienylacetylene **7a** with *t*BuLi produced a dithiolate intermediate **9**, which underwent the 5-*endo-dig* mode cyclization to give a thieno[3,2-*b*]thienylthiophenedithiolate (**10**).[21] The subsequent oxidative workup with $K_3[Fe(CN)_6]$ in a NaOH aqueous solution yielded the thieno[3,2-*c*](1,2-dithiin) **8a** in 65% yield. The dechalcogenation of **8a** with copper nanopowder (ca. 100 nm mesh) was accomplished by heating at 300 °C for 20 min without solvent by using a sand bath. The extraction with dichloromethane gave the tetrathienoacene **6a** in 56% yield.



Scheme 2. Synthesis of tetrathienoacene **6a** and the plausible intermediates. Reagents and conditions: i) 1) *t*BuLi, THF; 2) S_8 (3.0 mol amt.); 3) $K_3[Fe(CN)_6]$, 1 N aq. NaOH. ii) Cu nanopowder, 300 °C.

On the basis of this procedure, hexathienoacene **6b** and octathienoacene **6c** were also successfully synthesized, as shown in Scheme 3. Thus, starting from the bis(thienothienyl)acetylene **7b**, the intramolecular double cyclization gave the fused 1,2-dithiin **8b** in 42% yield. This compound was further converted into the hexathienoacene **6b** in 60% yield by the dechalcogenation. On the other hand, the cyclization of a diacetylenic starting material **7c** also simultaneously proceeded at the two acetylene moieties to give three regioisomers (in terms of the positions of the 1,2-dithiin rings) of fused bis(1,2-dithiin) **8c**, all of which were collected as a mixture in 46% yield and subjected to the subsequent dechalcogenation without further purification, since the dechalcogenation of each isomer yields an identical product. In fact, a treatment of the mixture with copper nanopowder gave the octathienoacene **6c** in 51% yield as the sole product.



Scheme 3. Synthesis of a) hexathienoacene **6b** and b) octathienoacene **6c**. Reagents and conditions: i) 1) *t*BuLi, THF; 2) S_8 (3.0 mol amt.); 3) $K_3[Fe(CN)_6]$, 1 N aq. NaOH. ii) Cu nanopowder, 300–340 °C.

There are several important points about the present procedure.

1) The intramolecular double cyclization of the bis(*o*-haloaryl)acetylenes is a monoacetylenic version of the previously reported triple cyclization,[18a] in which the 1,4-bis(*o*-haloaryl)diacetylenes can be converted into the corresponding two aryl-ring-fused dithieno[3,2-*c*:2′,3′-*e*](1,2-dithiin) derivatives through the similar reaction pathway to the present one. One advantage of using the acetylenic starting materials instead of the previous diacetylenic compounds is the readily availability of the extended starting materials like **7c**, which can be easily synthesized by the iterative Sonogashira reaction/alkaline desilylation procedure starting from appropriate arylhalides with trimethylsilylacetylene.
2) It is also worth noting that the present procedure is complementary to the previous one in terms of the number of rings found in the produced fused oligothiophenes. Thus, while the previous method converts the 3-halothienyl-substituted symmetrical diacetylenes into the fused oligothiophenes with an odd number of thiophene rings, such as the pentathienoacenes, in the present procedure the 3-halothienyl-substituted symmetrical monoacetylenes are transformed into the even numbered ring-fused oligothiophenes.
3) The silyl groups at the terminal positions of the starting materials play important roles not only to retain the solubility of the products in common solvents, but also to let the double cyclization cleanly proceed. Without the silyl groups, the cyclization only resulted in a complex mixture of products, probably due to the high reactivity at the 5-position of the thiophene ring.

The produced fused oligothiophenes have a high thermal stability. According to the thermogravimetric analysis, for instance, the decomposition temperature for a 5 % weight loss (T_d5) of the octathienoacene **6c** is 390 °C. While the silyl-substituted fused oligothiophenes have a good solubility up to the hexathienoacene **6b**, the octathineoacene **6c** has a rather poor solubility (0.09 mg mL^{-1} in THF).

Photophysical properties of fused oligothiophenes: The UV/Vis absorption and fluorescence spectra of the series of fused oligothiophenes are shown in Figure 1 and their data are summarized in Table 1.

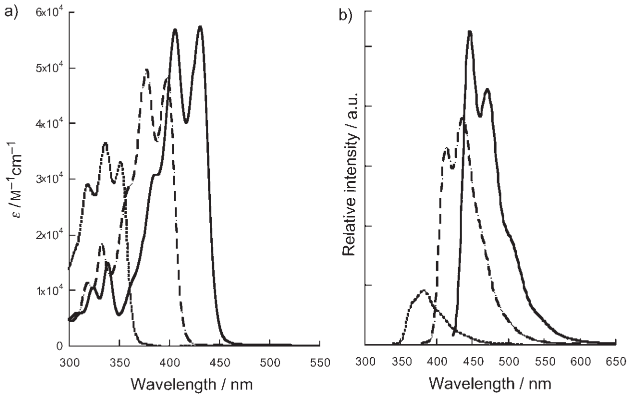


Figure 1. Photophysical properties of the fused oligothiophenes: a) UV/Vis absorption and b) fluorescence spectra in *o*-dichlorobenzene: **6a**, dotted line; **6b**, dashed line; **6c**, solid line.

Table 1. Photophysical data for fused oligothiophenes.

	Absorption[a]		Fluorescence[a]		Stokes shift
	λ_{max} [nm][b]	log ε	λ_{max} [nm][b]	Φ_F[c]	$\Delta\lambda_{max}$ [cm^{-1}]
6a	352	4.52	368 (sh)[d]	0.08	1230
6b	398	4.68	414[d]	0.32	970
6c	431	4.76	447	0.39	830

[a] In *o*-dichlorobenzene. [b] Only the longest absorption and shortest emission maximum wavelengths are given. [c] Determined using quinine sulfate in 0.5 M H_2SO_4 aqueous solution as a standard. [d] The highest emission bands are located at 382 nm for **6a** and 437 nm for **6b**.

In the absorption spectra, all the fused oligothiophenes show vibronically structured absorption bands. Their longest absorption maximum wavelength red-shifts by about 80 nm from 352 nm for **6a** to 431 nm for **6c**, associated with a slight increase in the molar absorption coefficient. In the fluorescence spectra, as the π conjugation is extended, the emission maximum shifts to longer wavelength from 368 nm for **6a** to 447 nm for **6c** and the fluorescence quantum yield also increases from 0.08 for **6a** to 0.39 for **6c**. Notably, both of the absorption and emission maximum wavenumbers show good linear relationships with the reciprocal number (1/*n*) of thiophene rings, as shown in Figure 2. Extrapolation of the linear plots to $1/n = 0$ estimates the absorption and emission maxima for the polythienoacenes to be 552 and 566 nm, respectively, which are consistent with the values obtained from the odd-numbered thiophene-ring-containing fused oligothiophenes, as reported by Matzger and co-workers.[11] The other notable fact is that the Stokes shift decreases from 1230 cm^{-1} for **6a** to 830 cm^{-1} for **6c**, indicative of a smaller structural difference between the ground state and the excited state, as the π conjugation is extended.

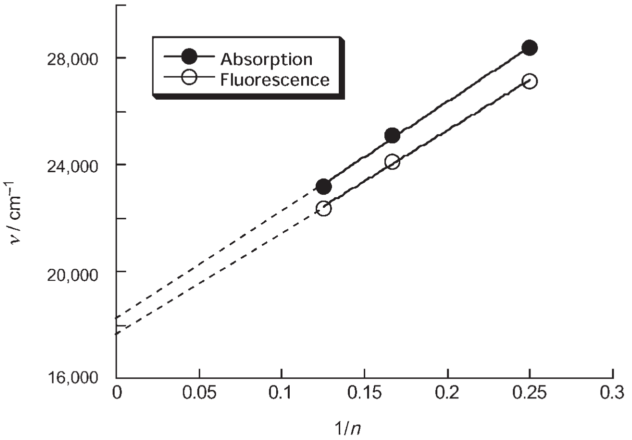


Figure 2. Plots of absorption and fluorescence maxima of fused oligothiophenes **6** as a function of the reciprocal number of thiophene rings.

Electrochemical properties of fused oligothiophenes: To obtain a deeper insight into the behavior of the fused oligothiophenes against oxidation, their electrochemical properties were studied by cyclic voltammetry. All the fused oligothiophenes **6**, which have silyl groups at the terminal positions, show reversible oxidation waves, as shown in Figure 3, indicative of the significant stability of the produced cationic species in these rigid ladder skeletons. Notably, their first oxidation potentials also show a linear dependence on the reciprocal number of thiophene rings, as shown in Figure 4. The extrapolation of the linear plot indicates that the oxidation potential will decrease up to 0.14 V (vs. ferrocene/ferrocenium) upon infinitely extending the π conjugation. While the tetrathienoacene **6a** and hexathienoacene **6b** only show the first oxidation process, the octathienoacene **6c** exhibits a second oxidation wave, demonstrating that the extension of the π conjugation with more than eight fused thiophene rings allows the formation of the dication. In fact, upon chemical oxidation by treating **6c** with an excess amount of $NO^+SbF_6^-$ as an oxidant, we have succeeded in obtaining its dicationic complex **6c**$[SbF_6]_2$ as air-sensitive golden crystals, the structure of which was determined by the X-ray crystallography (vide infra).

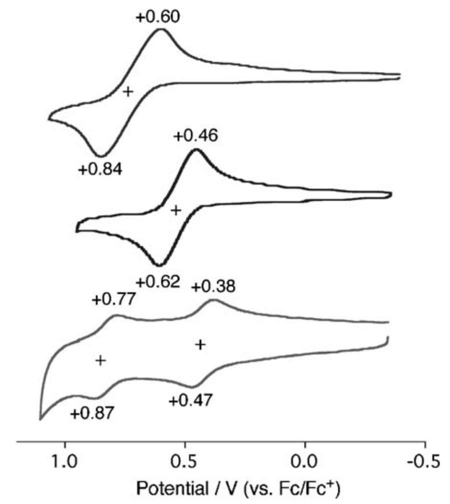


Figure 3. Cyclic voltammograms of fused oligothiophenes of **6a** (top), **6b** (middle), and **6c** (bottom). Measurement conditions: $n\mathrm{Bu_4NPF_6}$ (0.1 M) in *o*-dichlorobenzene; scan rate 50 $mV\,s^{-1}$.

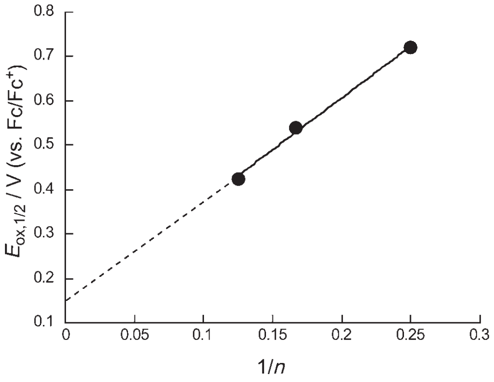


Figure 4. Plot of the first oxidation potential of fused oligothiophenes **6** as a function of the reciprocal number of thiophene rings.

Crystal structures of octathienoacence and its dication: Crystal structures of the octathienoacene **6c** and its dication **6c**$[SbF_6]_2$ were determined by the X-ray crystallography. Their structural data are summarized in Table 2, and their ORTEP drawings are shown in Figure 5. Both compounds have nearly flat π-conjugated frameworks with the length of approximately 1.8 nm. For example, the dihedral angle between the two outermost thiophene rings is only 6.9° for **6c** and 0° for **6c**$[SbF_6]_2$.

The degree of bond alternation in the π-conjugated framework is important for discussing the nature of the π system. Figure 6 shows the plots of the bond length versus the bond number in the octathienoacene framework. In the neutral **6c**, there is substantial bond alternation. The odd-numbered bonds are shorter than the even-numbered bonds and their averaged difference is about 0.04 Å, which is com-

Table 2. Structural data for **6c** and **6c**[SbF$_6$]$_2$.

	6c	**6c**[SbF$_6$]$_2$
bond distances [Å]		
C1–C2	1.372(5)	1.373(11)
C2–C3	1.412(5)	1.398(10)
C3–C4	1.379(5)	1.397(10)
C4–C5	1.427(5)	1.375(10)
C5–C6	1.379(5)	1.414(10)
C6–C7	1.419(5)	1.386(10)
C7–C8	1.385(5)	1.437(10)
C8–C9 (C9*)	1.420(5)	1.364(10)
C9–C10 (C9*)	1.382(5)	1.452(14)
C1–S1	1.750(4)	1.752(7)
C4–S1	1.713(4)	1.743(8)
C3–S2	1.748(4)	1.718(8)
C6–S2	1.732(4)	1.753(7)
C5–S3	1.731(4)	1.734(7)
C8–S3	1.737(4)	1.717(8)
C7–S4	1.732(4)	1.723(8)
C10 (C9)–S4	1.737(4)	1.748(7)
bond angles [°]		
C1-C2-C3	112.8(3)	115.3(6)
C2-C3-C4	114.0(3)	111.9(7)
C3-C4-C5	112.2(3)	113.3(7)
C4-C5-C6	112.1(3)	111.6(6)
C5-C6-C7	111.7(3)	112.4(6)
C6-C7-C8	112.4(3)	109.4(7)
C7-C8-C9 (C9*)	112.0(3)	110.9(7)
C8-C9 (C9*)-C10 (C9)	112.2(3)	112.9(8)
C1-S1-C4	92.58(17)	91.7(4)
C3-S2-C6	90.33(17)	89.7(3)
C5-S3-C8	90.16(17)	88.2(4)
C7-S4-C10 (C9)	90.35(17)	89.4(3)

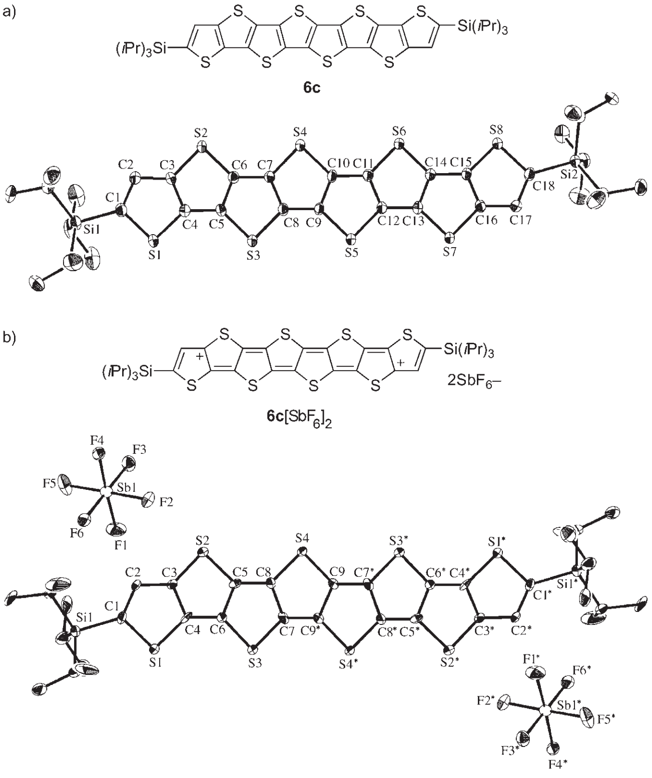


Figure 5. ORTEP drawing of a) octathienoacene **6c** and b) its dicationic complex **6c**[SbF$_6$]$_2$ (50 % probability for thermal ellipsoids).

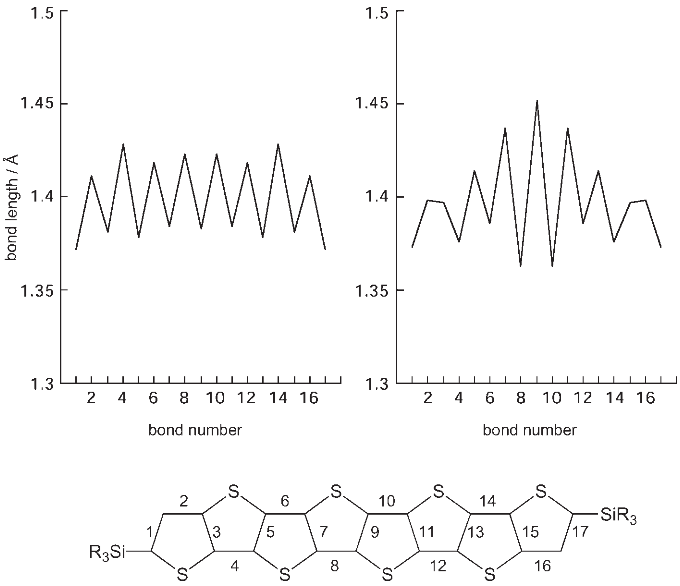


Figure 6. Comparison of bond alternation in the crystal structures of neutral **6c** (left) and dicationic complex **6c**[SbF$_6$]$_2$ (right).

parable to those in the non-fused oligothiophenes.[22,23] This result demonstrates that, unlike the acenes, the fused oligothiophenes have little contribution of the quinoid structure in the neutral state, and each thiophene ring retains a substantial aromaticity. In contrast, the dication **6c**[SbF$_6$]$_2$ has a large quinoid structure. Thus, the even-numbered bonds are much shorter than the odd-numbered bonds and there are marked bond alternations of 0.02–0.09 Å, except for the bonds in the terminal thiophene rings. In the terminal thiophene rings, while the bond length of bond 1 is in the range of an ordinal C=C double bond, those of the bonds 2 and 3 are comparable to each other and slightly shorter than those of the other odd-numbered bonds. These facts suggest that the two cationic charges seem to mostly localize at the terminal thiophene rings, particularly at the C3 and C3* positions, as schematically shown in Figure 5. This structure is consistent with that expected by the theoretical calculations[16] and might be important as an experimental description of the bipolaron in the fused oligothiophene structure.

While in the crystal packing, the dication **6c**[SbF$_6$]$_2$ does not have any special intermolecular interaction, it is interesting to note that the neutral **6c** shows a distinct intermolecular S···S nonbonding interaction. Thus, as shown in Figure 7a, the **6c** molecule aligns in parallel and slightly overlaps with the neighboring molecules with the closest nonbonding S···S distance of 3.4 Å, which is shorter than the sum of the van der Waals radii of two sulfur atoms (3.6 Å). Consequently, **6c** forms a stairlike π sheet, as shown in Figure 7b, two of which pair up with an interplane distance of 7.0 Å. The space between the two sheets is filled with *o*-dichlorobenzene solvent molecules. Finally, the pairs of two π sheets are arranged in a herringbone-like packing structure, as shown in Figure 7c. It may be rationalized that the bulky triisopropylsilyl groups prevent the face-to-face π stacking,

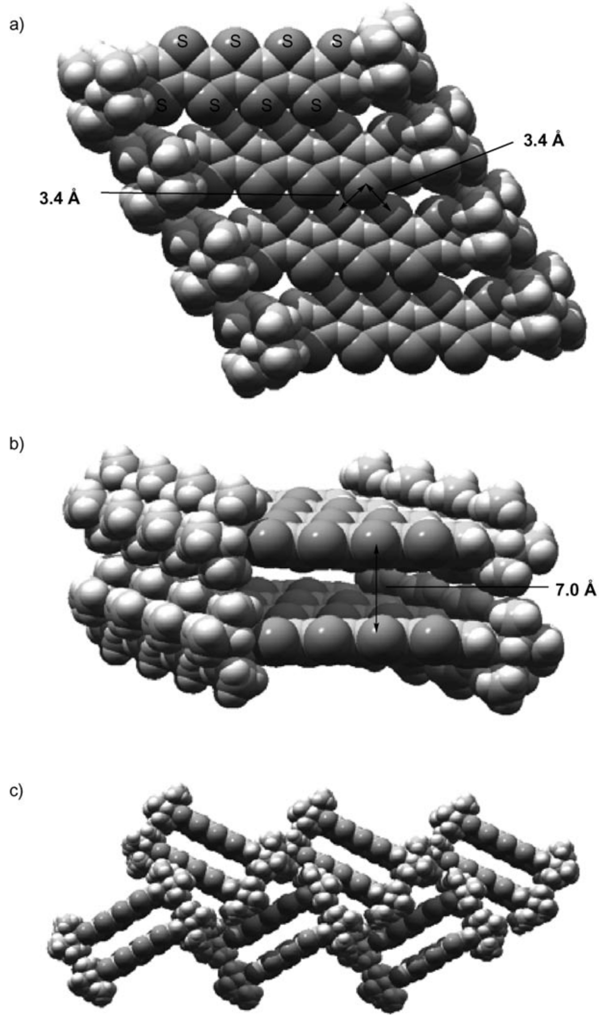


Figure 7. Crystal packing of octathienoacene **6c**: arrangements of a) molecules and b) π sheets, and c) a view of the packing structure along the *a* axis.

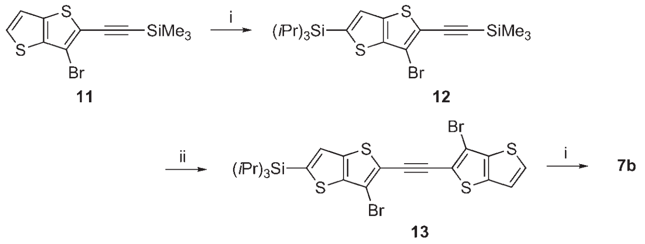
but the attractive nonbonding S···S interaction still exists, resulting in the formation of this packing structure.

Conclusion

We have described a general and versatile synthetic route to the extended fused oligothiophenes on the basis of the intramolecular double cyclization. This methodology enabled us to synthesize a series of derivatives consisting of an even number of thiophene rings, up to eight-ring fused octathienoacenes. Not only the absorption and emission maxima, but also the oxidation potentials show linear relationships with the reciprocal number of thiophene rings, indicative of the perfect extension of the π conjugation in this ladder framework. Reversible redox behavior is another notable feature for the present fused oligothiohenes that promise the potential use as a carrier transporting material in organic electronics. In addition, we have succeeded in the structural elucidation of the neutral and dicationic octathienoacenes, which provides us with important information about the electronic structures of the fused oligothiophenes. Further studies on the synthesis of a series of derivatives as well as their application in organic field-effect transistors are now in progress in our laboratory.

Experimental Section

General methods: Melting point (m.p.) determination was performed using a Yanaco MP-S3 instrument. ^{1}H and ^{13}C NMR spectra were measured with a JEOL EX-270 spectrometer, a JEOL A-400 spectrometer, or a VARIAN INOVA-500 spectrometer. UV/Vis absorption spectra and fluorescence spectra were recorded with a Shimadzu UV-3150 spectrometer and a F-4500 Hitachi spectrometer, respectively, in degassed spectral grade THF. Cyclic voltammetry were recorded on a CHI600 A instrument. Thin-layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using a Fuji Silysia silica gel PSQ60B (60 mm). Recycling preparative gel permeation chromatography (GPC) was performed by using polystyrene gel columns (JAIGEL 1H and 2H, Japan Analytical Industry) with toluene or chloroform as an eluent. Copper nanopowder (100 nm) was purchased from Aldrich. Compound **7b** was obtained according to Scheme 4. 3-Bromo-2-(trimethylsilylethynyl)thieno[3,2-*b*]thiophene (**11**) was prepared by Sonogashira coupling of 3-bromo-2-iodothieno[3,2-*b*]thiophene with trimethylsilylacetylene in the presence of $PdCl_2(PPh)_3$/CuI catalyst system in triethylamine. All reactions were carried out under argon atmosphere except where noted.



Scheme 4. Synthesis of compound **7b**. Reagents and conditions: i) LDA, (iPr)$_3$SiOTf, THF. ii) 1) K_2CO_3, THF/MeOH; 2) 2-bromothieno[3,2-*b*]thiophene, [$PdCl_2(PPh_3)_2$], CuI, Et_3N.

Bis(3-bromo-5-trimethylsilyl-2-thienyl)acetylene (7a): a solution of *n*BuLi in hexane (1.60 M, 21.8 mL, 34.8 mmol) was added dropwise to a solution of diisopropylamine (5.43 mL, 38.3 mmol) in THF (38 mL) at −78 °C. After stirring for 15 min, the solution was allowed to warm to 0 °C over 20 min. The produced solution of lithium diisopropylamide was added dropwise to a solution of 1,2-bis(3-bromo-2-thienyl)acetylene (5.50 g, 15.8 mmol) and trimethylsilyl chloride (4.12 g, 37.9 mmol) in THF (80 mL) at −78 °C. After stirring for 1 h, the mixture was gradually warmed to room temperature over 5 h. The mixture was quenched with a 1 M NH_4Cl aqueous solution (50 mL), and extracted with diethyl ether. The organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting mixture was subjected to a silica gel column chromatography (hexane, $R_f = 0.49$) to give 7.59 g (15.4 mmol) of **7a** in 98 % yield as pale yellow solid. M.p. 86–87 °C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.08$ (s, 2H), 0.32 ppm (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 144.60$, 136.21, 124.73, 117.50, 89.23, −0.47 ppm; MS (EI): m/z: 492 $[M]^+$; elemental analysis calcd (%) for $C_{16}H_{20}Br_2S_2Si_2$: C 39.02, H 4.09; found: C 39.18, H 4.15.

3-Bromo-5-triisopropylsilyl-2-(trimethylsilylethynyl)thieno[3,2-*b*]thiophene (12): A solution of lithium diisopropylamide in THF, freshly prepared from diisopropylamine (0.95 mL, 6.69 mmol) and *n*BuLi (1.58 M hexane solution, 4.0 mL, 6.37 mmol) in THF (6.7 mL), was added dropwise to a solution of 3-bromo-2-(trimethylsilylethynyl)thieno[3,2-*b*]thiophene (1.83 g, 5.79 mmol) and triisopropylsilyl trifluoromethanesulfonate (8.87 g, 29.0 mmol) in THF (29 mL) at −78 °C. After stirring for 80 min, the mixture was gradually warmed to room temperature with stirring over 2 h. The mixture was quenched with a 1 M NH_4Cl aqueous solution, and extracted with diethyl ether. The organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting mixture was subjected to a silica gel column chromatography (hexane, $R_f = 0.59$) to give 2.21 g (4.69 mmol) of **12** in 81 % yield as pale yellow solid. M.p. 101–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.34$ (s, 1H), 1.29–1.42 (m, 3H), 1.14 (d, J = 7.2 Hz, 18H), 0.31 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 144.66$, 141.53, 138.70, 127.48, 121.94, 108.77, 104.65, 96.54, 18.52, 11.76, −0.17 ppm; HRMS (EI): m/z calcd for $C_{20}H_{31}BrS_2Si_2$: 470.0589; found: 470.0588.

[3-Bromo-5-(triisopropylsilyl)-2-thieno[3,2-*b*]thienyl](3-bromo-2-thieno-[3,2-*b*]thienyl)acetylene (13): Potassium carbonate (37.5 mg, 0.271 mmol) was added to a solution of **12** (1.28 g, 2.71 mmol) in a 1:1 THF/methanol mixed solvent (16 mL) at room temperature. The mixture was stirred for 2 h, and then concentrated under reduced pressure. After addition of a 1 M NH_4Cl aqueous solution, the mixture was extracted with diethyl ether. The organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated to give 1.08 g (2.70 mmol) of 3-bromo-2-ethynyl-5-(triisopropylsilyl)thieno[3,2-*b*]thiophene in 99 % yield as pale orange solid. This compound was used for the next reaction without further purification: ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.33$ (s, 1H), 3.69 (s, 1H), 1.31–1.42 (m, 3H), 1.12 ppm (d, $J = 7.3$ Hz, 18H). A solution of the produced 3-bromo-2-ethynyl-5-(triisopropylsilyl)thieno[3,2-*b*]thiophene (1.08 g, 2.71 mmol) in toluene (6.3 mL) was added dropwise to a solution of 3-bromo-2-iodothieno[3,2-*b*]thiophene (849 mg, 2.46 mmol), $[PdCl_2(PPh_3)_2]$ (17.3 mg, 0.0246 mmol) and CuI (9.4 mg, 0.0492 mmol) in diisopropylamine (12.4 mL) at room temperature. The mixture was stirred for 12 h at the same temperature. Insoluble salts were removed by filtration with a Celite, and washed with benzene. The filtrate was concentrated under reduced pressure. The mixture was passed through a silica gel column (dichloromethane) and further purified by recycling preparative gel permeation chromatography (toluene as an eluent) to give 1.28 g (2.07 mmol) of **13** in 84 % yield as yellow solid. M.p. 136–138 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.56$ (d, $J = 5.4$ Hz, 1H), 7.37 (s, 1H), 7.28 (d, $J = 5.4$ Hz, 1H), 1.35–1.42 (m, 3H), 1.14 ppm (d, $J = 7.3$ Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 145.07$, 142.12, 139.63, 138.18, 130.09, 127.54, 121.06, 120.86, 120.37, 90,46, 90.22, 18.54, 11.77 ppm; MS (EI): m/z: 616 $[M]^+$; elemental analysis calcd (%) for $C_{23}H_{24}Br_2S_4Si$: C 44.80, H 3.92; found: C 45.06, H 3.92.

Bis(3-bromo-5-triisopropylsilyl-2-thieno[3,2-*b*]thienyl)acetylene (7b): A solution of lithium diisopropylamide in THF, freshly prepared from diisopropylamine (0.15 mL, 1.03 mmol) and *n*BuLi (1.58 M hexane solution, 0.62 mL, 0.98 mmol) in THF (1.0 mL), was added dropwise to a solution of **13** (601 mg, 0.98 mmol) and triisopropylsilyl trifluoromethanesulfonate (359 mg, 1.17 mmol) in THF (10 mL) at −78 °C. After stirring for 1 h, the mixture was gradually warmed to room temperature over 3.5 h. The mixture was quenched with a 1 M NH_4Cl aqueous solution, and extracted with dichloromethane. The organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting mixture was passed through a silica gel column (dichloromethane) and further purified by recycling preparative gel permeation chromatography (toluene as an eluent) to give 350 mg (0.45 mmol) of **7b** in 46 % yield as yellow solid. M.p. 268–270 °C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.36$ (s, 2H), 1.33–1.41 (m, 6H), 1.14 ppm (d, $J = 7.3$ Hz, 36H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 142.04$, 139.59, 129.03, 127.55, 121.17, 109.07, 90.56, 18.54, 11.78 ppm; HRMS (EI): m/z calcd for $C_{32}H_{44}Br_2S_4Si_2$: 772.0212; found: 772.0217.

3,6-Dibromo-2,5-bis[(3-bromo-5-triisopropylsilyl-2-thienyl)ethynyl]thieno[3,2-*b*]thiophene (7c): A solution of 3-bromo-5-triisopropylsilyl-2-thienylacetylene (4.83 g, 14.1 mmol) in toluene (10 mL) was added dropwise to a mixture of 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene (3.05 g, 6.70 mmol), $[PdCl_2(PPh_3)_2]$ (94 mg, 0.134 mmol), and CuI (51 mg, 0.268 mmol) in a 5:2 triethylamine/toluene mixed solvent (70 mL) at room temperature. The mixture was stirred at 70 °C for 18 h. The mixture was quenched with a 1 N HCl aqueous solution, and extracted with toluene. The organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Recrystallization from a 1:3 toluene/ethyl acetate mixed solvent gave 1.42 g (1.45 mmol) of **7c** as yellow crystals. The residue was further purified by a silica gel column chromatography (hexane, $R_f = 0.55$) to give 1.61 g (1.64 mmol) of **7c**. In total, 3.03 g (3.09 mmol) of **7c** was obtained in 46 % yield. M.p. 179–180 °C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.13$ (s, 2H), 1.26–1.40 (m, 6H), 1.11 ppm (d, $J = 7.3$ Hz, 36H); ^{13}C NMR (68 MHz, C_6D_6): $\delta = 140.39$, 139.26, 138.11, 125.16, 123.91, 118.99, 109.92, 92.43, 90.38, 18.70, 11.98 ppm; HRMS (FAB): m/z calcd for $C_{36}H_{44}Br_4S_4Si_2$: 975.8598; found:975.8609.

A typical procedure for the intramolecular double cyclization—compound 8a: A solution of *t*BuLi in pentane (1.53 M, 26.5 mL, 40.6 mmol) was added dropwise to a solution of compound **7a** (5.0 g, 10.2 mmol) in THF (100 mL) at −78 °C. After being stirred for 1 h, sulfur (976 mg, 30.5 mmol) was added as a crystal under a stream of argon. The mixture was kept at the same temperature for 5 min and then allowed to warm to room temperature with stirring over 2 h. The mixture was quenched with a 1 M sodium hydroxide aqueous solution, followed by addition of $K_3[Fe(CN)_6]$ (13.4 g, 40.6 mmol). The resulting mixture was extracted with diethyl ether for three times. The combined organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting mixture was subjected to a silica gel column chromatography (hexane, $R_f = 0.54$) to give 2.83 g (6.61 mmol) of **8a** in 65 % yield as red oil. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.33$ (s, 1H), 7.08 (s, 1H), 0.37 (s, 9H), 0.34 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): d 144.94, 143.02, 139.67, 139.53, 138.24, 136.10, 132.72, 125.53, 125.33, 116.10, −0.27, −0.33 ppm; HRMS(EI): m/z calcd for $C_{16}H_{20}S_5Si_2$: 427.9707; found: 427.9708.

Compound 8b: This compound was obtained essentially in the same manner as described for **8a** starting from **7b** in 42 % yield as a red powder. M.p. 142–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.41$ (s, 1H), 7.36 (s, 1H), 1.45–1.34 (m, 6H), 1.16–1.14 ppm (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 143.48$, 143.37, 141.03, 139.90, 138.59, 138.08, 136.58, 135.79, 134.70, 134.43, 128.25, 127.06, 126.58, 117.29, 115.87, 18.56, 18.54, 11.81, 11.78 ppm; HRMS(EI): m/z calcd for $C_{32}H_{44}Si_2S_7$: 708.1026; found: 708.1017.

Compound 8c (as a mixture of three regioisomers): A solution of *t*BuLi in pentane (1.43 M, 5.9 mL, 8.42 mmol) was added dropwise to a solution of compound **7c** (1.03 g, 1.05 mmol) in THF (40 mL) at −78 °C. After stirring for 1.5 h, sulfur (810 mg, 25.3 mmol) was added as a crystal under a stream of argon. The mixture was kept at the same temperature for 5 min and then allowed to warm to room temperature with stirring over 2.5 h. The mixture was quenched with $K_3[Fe(CN)_6]$ in a 1 M sodium hydroxide aqueous solution. The mixture was extracted with diethyl ether. The organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting mixture was subjected to a silica gel column chromatography (hexane, $R_f = 0.36$). Further purification by a recycling preparative gel permeation chromatography (chloroform as an eluent) gave 416 mg (0.488 mmol) of **8c** as a mixture of three regioisomers in 46 % yield as purple powders. This mixture was directly used for the subsequent dechalcogenation without further separation of each isomer. M.p. 235 °C (decomp); ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.41$ (s), 7.37 (s), 7.35 (s), 7.10 (s), 1.47–1.34 (m), 1.16–1.13 ppm (m); MS(MALDI): m/z: 852 $[M]^+$.

A typical procedure for dechalcogenation—compound 6a: The mixture of **8a** (300 mg, 0.70 mmol) and copper nanopowder (178 mg, 2.80 mmol) was heated at 300 °C for 20 min using a sand bath. The reaction mixture was dissolved into CH_2Cl_2, and the insoluble materials were removed by filtration with a Celite. The filtrate was concentrated under reduced pressure and the resulting mixture was subjected to a silica gel column chromatography (hexane, $R_f = 0.45$) to give 155 mg (0.391 mmol) of **6a** in 56 % yield as a colorless powder. M.p. 200–202 °C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.38$ (s, 2H), 0.38 ppm (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 142.58$, 142.27, 136.83, 132.90, 126.69, 100.55, −0.16 ppm; MS

(EI): m/z: 396 $[M]^+$; elemental analysis calcd (%) for $C_{16}H_{20}S_4Si_2$: C 48.44, H 5.08; found: C 48.50, H 5.00.

Compound 6b: This compound was obtained essentially in the same manner as described for **6a** starting from **8b** in 60% yield as white solid. M.p. 283–284 °C; ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.41$ (s, 2H), 1.46–1.35 (m, 6H), 1.17–1.14 ppm (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 142.11, 137.11, 136.75, 134.04, 132.31, 131.00, 128.18, 18.58, 11.81 ppm; HRMS (EI): m/z calcd for $C_{32}H_{44}Si_2S_6$: 676.1306; found: 676.1317.

Compound 6c: This compound was prepared essentially in the same manner as described for **6a** starting from **8c** (as a mixture of three regioisomers) and obtained in 51% yield by sublimation as yellow crystals. M.p. >300 °C; ^{1}H NMR (400 MHz, $[D_4]$-*o*-dichlorobenzene): $\delta = 7.28$ (s, 2H), 1.28–1.19 (m, 6H), 1.08 ppm (d, $J = 7.2$ Hz, 36H); HRMS(EI): m/z calcd for $C_{36}H_{44}Si_2S_8$: 788.0747; found:788.0750. ^{13}C NMR spectrum was not able to obtain due to its poor solubility.

Chemical oxidation of octathienoacene 6c: A mixture of **6c** (0.58 mg, 0.74 μmol) and $NO^+SbF_6^-$ (1 mg, 3.8 μmol) was placed in a Pyrex glass tube. Dichloromethane (0.75 mL) was transferred into the tube. The tube was evacuated and sealed. After sonication for 5 min, the tube was placed in a refrigerator at −30 °C for 12 h. Upon standing, golden crystals of **6c**$[SbF_6]_2$ were obtained.

X-ray crystallographic analysis of compound 6c: Single crystals of **6c** suitable for X-ray crystal analysis were obtained by recrystallization from a solution of **6c** in *o*-dichlorobenzene (ODCB). Intensity data were collected at 173 K on a Rigaku Single-Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and a graphite monochromater. A total of 34327 reflections were measured at a maximum 2θ angle of 50.0°, of which 8980 were independent reflections ($R_{int} = 0.0607$). The structure was solved by direct methods (SHELXS-97)[24] and refined by the full-matrix least-squares on F^2 (SHELXL-97).[24] Two ODCB molecules were included, one of which was disordered and was solved by using appropriate disordered models. Thus, for the ODCB molecule consisting of C43–C48 and Cl3, Cl4, two sets of chlorine atoms, that is, Cl3A, Cl4A and Cl3B, Cl4B, were placed and their occupancies were refined to be 0.55 and 0.45, respectively. This disordered molecule was restrained by DFIX instruction with fixed C–C and C–Cl bond lengths and also by using the ISOR instruction during refinement. All non-hydrogen atoms were refined anisotropically and all hydrogen atoms, except for those of the disordered ODCB, were placed by using AFIX instructions. The crystal data are as follows: $C_{48}H_{52}Cl_4S_8Si_2$; $M_r = 1083.36$, crystal size $0.20 \times 0.10 \times 0.05$ mm^3, monoclinic, $P2_1/c$, $a = 7.421(2)$, $b = 27.469(8)$, $c = 25.354(8)$ Å, $\beta = 96.159(4)°$, $V = 5138(3)$ Å^3, $Z = 4$, $\rho_{cald} = 1.400$ g cm^{-3}. The refinement converged to $R_1 = 0.0615$, w$R_2 = 0.1474$ $[I > 2\sigma(I)]$, GOF = 1.084.

X-ray crystal structure analysis of compound 6c$[SbF_6]_2$: Single crystals of **6c**$[SbF_6]_2$ suitable for X-ray crystal analysis were obtained by recrystallization from a solution of **6c**$[SbF_6]_2$ in dichloromethane in a sealed vacuum tube. Intensity data were collected at 100 K on a Rigaku Single-Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and graphite monochromater. A total of 10408 reflections were measured at a maximum 2θ angle of 50.0°, of which 5288 were independent reflections ($R_{int} = 0.0565$). The structure was solved by direct methods (SHELXS-97)[24] and refined by the full-matrix least-squares on F^2 (SHELXL-97).[24] Four solvent molecules of dichloromethane were included. Three isopropyl moieties of the triisopropylsilyl group consisting of C10–C18 were disordered and solved using appropriate disordered models. Thus, two sets of carbons, that is, C10A–C18A and C10B–C18B, were placed and their occupancies were refined to be 0.76 and 0.24, respectively. The two sets of disordered triisopropylsilyl groups (C10A–C18 and Si1), and (C10B–C18B and Si1) were restrained by SADI instruction as well as DELU instruction during refinement. All non-hydrogen atoms, except for the disordered isopropyl moieties of the triisopropylsilyl group consisting of C10B–C18B, were refined anisotropically and all hydrogen atoms were placed by using AFIX instructions. The crystal data are as follows: $C_{40}H_{52}Cl_8F_{12}S_8Sb_2Si_2$; $M_r =$ 1600.58, crystal size $0.05 \times 0.05 \times 0.01$ mm^3, triclinic, $P\bar{1}$, $a = 9.165(4)$, $b =$ 10.862(4), $c = 15.599(6)$ Å, $\alpha = 83.285(11)$, $\beta = 89.482(12)$, $\gamma = 84.235(11)°$, $V = 1534.3(10)$ Å^3, $Z = 1$, $\rho_{cald} = 1.732$ g cm^{-3}. The refinement converged to $R_1 = 0.0591$, w$R_2 = 0.1219$ $[I > 2\sigma(I)]$, GOF = 1.098.

CCDC-615569 and 615570 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_requeat/cif.

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