1,1,4,4-Tetra(2-furyl, 2-thienyl, and 2-selenienyl)butatrienes: Synthesis, Properties, and Molecular Structures[1]

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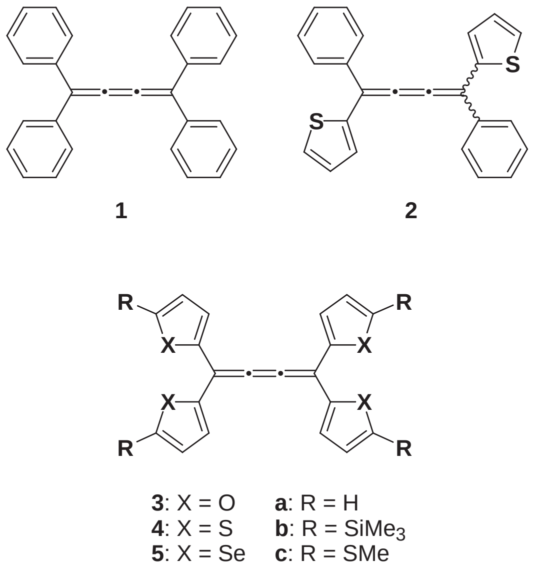
Tetra(2-furyl, 2-thienyl, and 2-selenienyl)butatrienes and their derivatives have been prepared by dimerization of ate-type complexes derived from the corresponding 1,1-dichloro-2,2-diarylethenes using appropriate copper complexes in moderate to high yields. These new butatrienes are relatively stable crystalline substances with intense absorption bands at long wavelengths. The electronic properties of the substituents at the 5-position of aryl groups remarkably influence the wavelength of the longest absorption and the π-electron distribution of butatriene moiety. Their redox potentials, measured by cyclic voltammetry, have higher amphoteric redox properties than those of tetraphenylbutatriene. The crystal structures of tetrakis(5-trimethylsilyl)-substituted derivatives show the following two features: (1) the thiophene and selenole derivatives have pseudo-D_2 structures, while the furan derivative has a C_2 symmetric structure probably due to the counterbalance between the energy of conjugation and the nonbonded chalcogen–chalcogen interaction; (2) the central double bonds of these butatrienes are considerably short.

Since tetraphenylbutatriene **1** was synthesized through dehydrohalogenation of 1,1,4,4-tetraphenyl-2,3-dichloro-2-butene by Brand in 1921,[2] several tetraarylbutatrienes have been prepared.[3–11] However, butatriene derivatives with five-membered heteroaromatics in place of the phenyl groups have received little attention except for a report on 1,4-diphenyl-1,4-di(2-thienyl)butatriene (**2**) by Kuhn and Jahn in 1953.[12] Recently, we have pointed out that 2-thienyl group stabilizes not only the positive but also negative charge on an adjacent carbon, which may indicate that the π-electron systems having 2-thienyl groups gain highly amphoteric redox properties.[13–17] In addition, the 2-thienyl group provides a reactive site to expand the π-electron system, because the 5-position of 2-thienyl group is easily lithiated by treatment with a base.[18–20] Moreover, 2-furyl and 2-selenienyl groups have been known to possess basically similar electronic properties. In this context, we have studied tetra(2-furyl, 2-thienyl, and 2-selenienyl)butatrienes **3**–**5** from synthetic, physicochemical, and structural points of view.

In 1986, we have reported that cyclooligomerization of the ate complexes derived from 1,1-dihalo-2,2-diarylethenes and appropriate copper reagents yielded the corresponding octaaryl[4]radiarenes together with tetraarylbutatrienes.[21] We reasoned from the results that the corresponding dihaloethenes **6**–**8** could serve as promising precursors for the title butatrienes (Chart 1).



1 **2**

3: X = O **a**: R = H
4: X = S **b**: R = SiMe$_3$
5: X = Se **c**: R = SMe

Chart 1.

Results and Discussion

Synthesis and Functionalization of Tetraarylbutatrienes. A thiophene derivative, 1,1-dichloro-2,2-di(2-thienyl)ethene (**7a**), was the only known compound used as a precursors; however, the reported synthesis from di(2-thienyl)diazomethane was unsatisfactory because of the low yield.[22] Thus, we examined Isaac's dichloromethylenation of diaryl ketones **9a**, **10a**, and **11a** using PPh$_3$–CCl$_4$.[23] The reactions successfully afforded dichloroethenes **6a**, **7a**, and **8a** in good yields, respectively. Thiophene and selenole derivatives, **7a** and **8a**, are regioselectively lithiated either at the 5-positions of the heterocycles or at the dichloromethylene carbons using the appropriate lithiating agent. Using lithium diisopropylamide (LDA), the heterocycles of **7a** and **8a** can be readily dilithiated, and the resulting dilithium compounds were quenched with proper electrophiles to give disubstituted derivatives **7b**, **7c**, and **8b**, respectively, in good yields. Lithiation of **6a** by LDA, however, was unsuccessful because of the relatively low acidity of 2-furyl groups. Bis(trimethylsilyl) derivative **6b** was thus synthesized by using dichloromethylenation of bis(2-trimethylsilylfuryl)methanone **9b**, prepared from 2-trimethylsilylfuran as a starting material. On the other hand, treatment of the dichloro-

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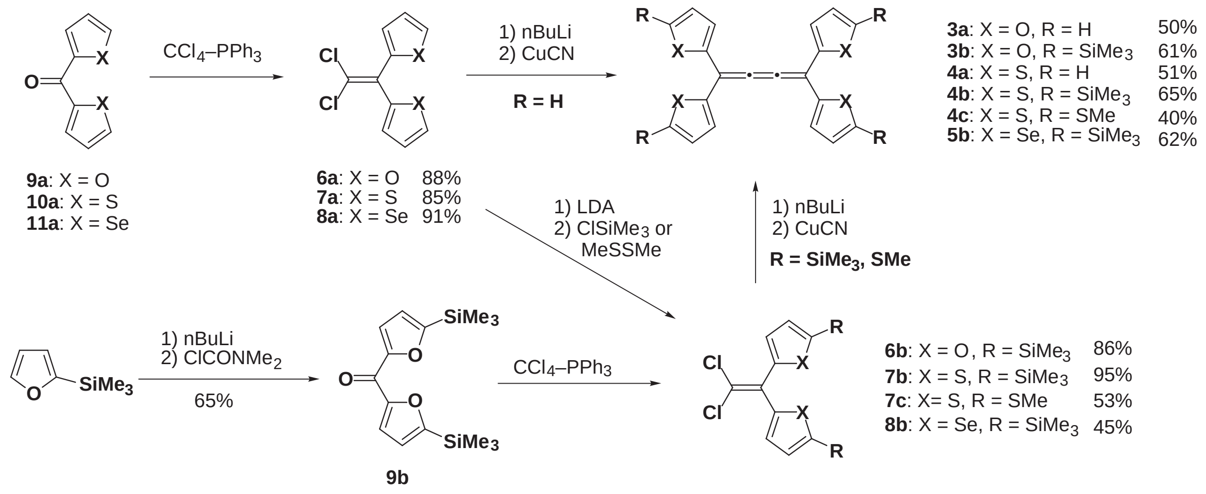

Scheme 1.

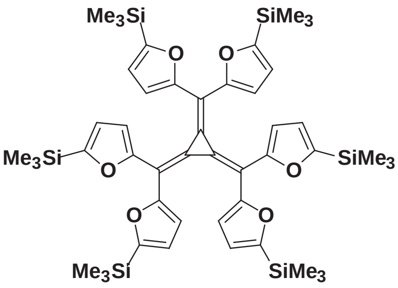

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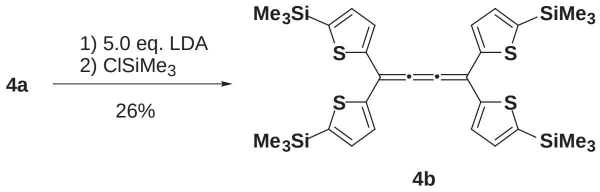
Chart 2.

ethenes **6**–**8** with butyllithium at −90 °C led to halogen–lithium exchange at the 1-position, affording the corresponding lithium carbenoids.[24] When the resulting solutions were allowed to warm to room temperature, the diarylacetylenes were afforded in good yields through the Fritsch-Buttenberg–Wiechell rearrangement.[25–27]

Several copper complexes ($CuBr\cdot SMe_2$, $CuI\cdot PBu_3$, $CuCl_2\cdot 2LiCl$, and CuCN) were examined for cyclooligomerization of the ate complex from **7a**. CuCN and $CuBr\cdot SMe_2$ gave satisfactory results; tetra(2-thienyl)butatriene **4a** was obtained in 51% yield. Then, the reactions of **6a** and **6b**, **7b** and **7c**, and **8b** were carried out using CuCN and $CuBr\cdot SMe_2$ to afford the butatrienes **3a** and **3b**, **4b** and **4c**, and **5b** in moderate to high yields, respectively. In the case of **8a**, **5a** formed as a minor component in the mixture of products and could not be isolated by silica-gel chromatography because it gradually decomposed on silica gel. The oligomerization of a copper carbenoid derived from **6b** and CuCN gave [3]radiarene **12** (Chart 2) in 2% yield together with **3b** in 61% yield. Except for the example, the procedure provided no radialene derivatives probably due to the electron-releasing ability of the heteroaryl groups.[15] These reactions are summarized in Scheme 1.

Tetralithiation and functionalization at the 5-positions of **4a** was successful using a suitable quenching reagent. The reaction of LDA (5.0 equiv) and **4a** in the presence of chlorotrimethylsilane in THF at −78 °C led to tetrasilylation giving **4b** in 26% yield (Scheme 2). The reaction may proceed stepwise, because tetradeuteration of **4a** using CH_3COOD as a quencher was incomplete.



Scheme 2.

Table 1. Selected Spectral Data of Butatrienes

	^{13}C NMR chemical shifts[a)]		Longest absorption maxima[b)]	Raman[c)] $\nu_{C=C}/cm^{-1}$
	sp carbon	sp^2 carbon		
3a	136.30	100.59	501 (4.73)	2034
3b	135.09	100.76	545 (4.80)	2039
4a	140.53	108.95	501 (4.54)	2035
4b	139.90	108.91	530 (4.79)	2023
4c	138.89	108.50	562 (4.59)	2032
5b	138.41	113.25	552 (4.68)	2025
1	151.9[d)]	122.6[d)]	419 (4.51)	2037

a) 67.8 MHz, δ/ppm in $CDCl_3$. b) λ_{max}/nm (log ε) in CH_2Cl_2. c) KBr disk. d) Ref. 4.

Spectral Data of the Butatrienes. Selected UV–vis, Raman, and ^{13}C NMR spectroscopic data of **3a** and **3b**, **4a**–**4c**, and **5b** together with those of **1** are listed in Table 1. These butatrienes with red to reddish purple color absorb at considerably longer wavelengths ($\lambda_{max} = 500$–560 nm) than yellow **1** (419 nm). From a comparison of the three tetrakis(trimethylsilyl) derivatives **3b**, **4b**, and **5b**, variation of the heteroatoms has little effect on the longest absorptions ($\Delta\lambda_{max} < 22$ nm). On the other hand, substitution at the 5-position of the aryl groups causes relatively large bathochromic shift; the longest absorption maxima of **4b** and **4c** are 29 and 61 nm longer than that of **4a**, respectively. In the Raman spectra, the C=C stretchings of these butatrienes are in a very narrow range (2023 to 2039 cm^{-1}), and no significant tendency is evident in relation to the different heterocycles. ^{13}C NMR spectra reveal that the sp and sp^2 carbons of these butatrienes resonate

Table 2. Redox Potentials of Butatrienes **3b**, **4a**–**4c**, **5b**, and **1**[a)]

	E_1^{ox}	E_1^{red}	E_2^{red}	E_1^{sum}
3b	$0.93^{\text{b),c)}}$	−1.17	−1.78	2.10
4a	$0.98^{\text{b),c)}}$	−1.15	−1.64	2.13
4b	$1.01^{\text{b),c)}}$	−1.00	−1.40	2.01
4c	$0.54^{\text{b)}}$	−0.99	−1.29	1.53
5b	$0.99^{\text{b),c)}}$	−1.01	−1.36	2.00
1	$1.25^{\text{b),c)}}$	−1.42	−1.76	2.67

a) V vs Ag/AgCl in DMF using 0.1 mol dm^{-3} $n\text{Bu}_4\text{NClO}_4$ (Fc/Fc$^+$ = +0.44 V). b) Two electron waves. c) Peak potentials.

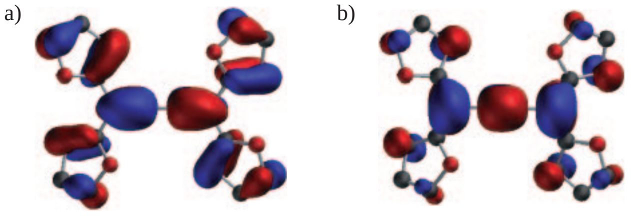
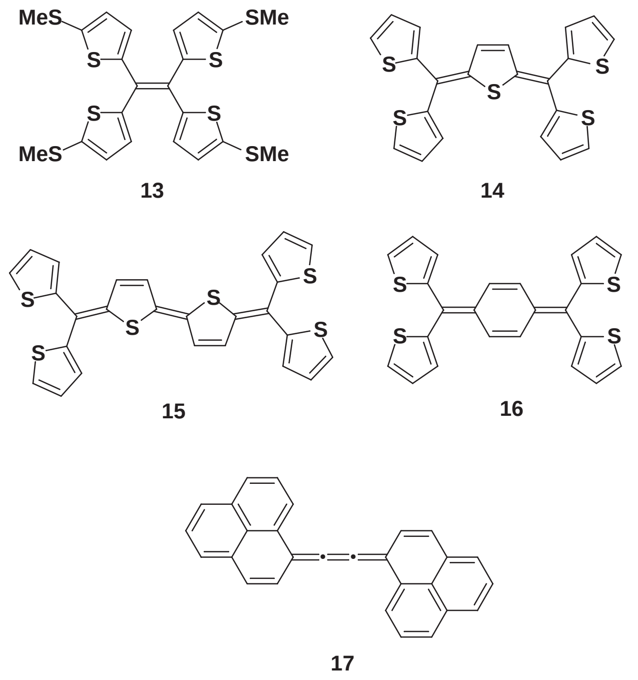

a) b)

Fig. 1. Molecular orbitals of **3a** calculated by PM3 method; a) HOMO, b) LUMO.

at higher magnetic field than those of **1**, and the chemical shifts of the sp^2 carbon are almost independent of the substituents but characteristic of the heteroaromatics. The order of the chemical shifts (**3** < **4** < **5**) is attributed to the electronic effects of the heteroatoms through σ-bond.

Electrochemical Properties. The cyclic voltammograms of the butatrienes **3b**, **4a**–**4c**, and **5b** had one pseudo-reversible two-electron oxidation wave and two reversible one-electron reduction waves. The redox potentials of these compounds together with those of **1** are listed in Table 2. All of the tetra(heteroaryl)butatrienes show higher electron-donating and electron-affinitive properties than **1**. While the redox potentials of **4b** and **5b** are quite similar to each other, the oxidation potential of **3b** ($E_1^{\text{ox}} = +0.93$ V) is slightly lower than that of **4b** ($E_1^{\text{ox}} = +1.01$ V), and the reduction potentials of **3b** ($E_1^{\text{red}} = -1.17$ V, $E_2^{\text{red}} = -1.78$ V) are more negative than those of **4b** ($E_1^{\text{red}} = -1.00$ V, $E_2^{\text{red}} = -1.40$ V). From these findings, it is thought that the stabilizing effect of the 2-furyl group on the adjacent positive charge is superior, but that on adjacent negative charge is inferior to those of 2-selenienyl and 2-thienyl groups. Semiempirical molecular orbital calculation (PM3) also supports this conclusion. Both HOMO and LUMO energy levels of **3a** are higher than those of **4a**, and the HOMO of **3a** consists of the furan rings as well as the butariene moiety, whereas LUMO of **3a** has little distribution on the furan rings (Fig. 1).

The substituent effects were examined in a series of thiophene derivatives **4a**–**4c**. Electron-withdrawing trimethylsilyl groups of **4b** increase the electron affinity compared with **4a** ($|\Delta E_1^{\text{red}}| = 0.15$ V, $|\Delta E_2^{\text{red}}| = 0.24$ V), but the change in oxidation potential is negligible ($|\Delta E_1^{\text{ox}}| = 0.02$ V). The methylthio derivative **4c** has considerably low oxidation and relatively high reduction potentials, indicating the ability of the methylthio group for stabilizing charge on an adjacent carbon. Tetrakis(5-methylthio-2-thienyl)ethene (**13**) has been known to exhibit a reversible two-electron process at 0.55 V and give a stable dication by chemical or electrochemical oxidation.[28] Moreover, the per(2-thienyl)-substituted quinodimethane derivatives **14**,[29] **15**,[13] and **16**[17] form stable and isolable dications. Though the oxidation potential of **4c** is comparable to that of **13**, the chemical oxidation of **4c** with NOBF$_4$ or Tl(CF$_3$COO)$_3$ only afforded polymeric materials. These results suggest that the expansion of π-system with two sp carbons provides little stabilization for the positive charge.



13 14 15 16 17

Chart 3.

On the other hand, the relatively high reduction potentials of **4c** suggest fairly large stabilization of the negative charges from π-expansion. Table 2 also shows the numerical sums of E^{ox} and E^{red}, i.e., $E^{\text{sum}} = E^{\text{ox}} + (-E^{\text{red}})$, which is an experimental measure for estimating the extent of amphoteric redox properties. The E_1^{sum} value of **4c** (1.53 V) is smallest among these heteroarylbutatrienes; butatriene **4c** should act as an amphoteric redox system, though it is inferior to 1,2-bis(1-phenalenylidene)ethene (**17**) ($E_1^{\text{sum}} = 1.34$ V), which is the best amphoteric redox system among the reported butatrienes (Chart 3).[30]

The X-ray Crystallographic Analyses of a Series of Tetrakis(trimethylsilyl) Derivatives 3b, 4b, and 5b. Tetrakis(trimethylsilyl) derivatives **3b**, **4b**, and **5b** crystallized from hexane solutions, and their molecular structures were determined by X-ray analysis. The crystallographic data are summarized in Table 3. ORTEP drawings of **3b**, **4b**, and **5b** are shown in Figs. 2, 3, and 4, respectively. Because the selenole derivative **5b** has two conformers in its unit cell (Fig. 4), the structures of each conformer are shown in Fig. 5. Selected bond lengths, bond angles, and torsion angles of these butatrienes are listed on Tables 4–6.

Compound of **3b** has C_2 symmetry and a propeller structure with an almost planar conformation (Fig. 2). The two different pairs of furan rings are twisted by 2.7° (ring 1) and 11.3° (ring 2) out of the butatriene plane. On the other hand, **4b** has

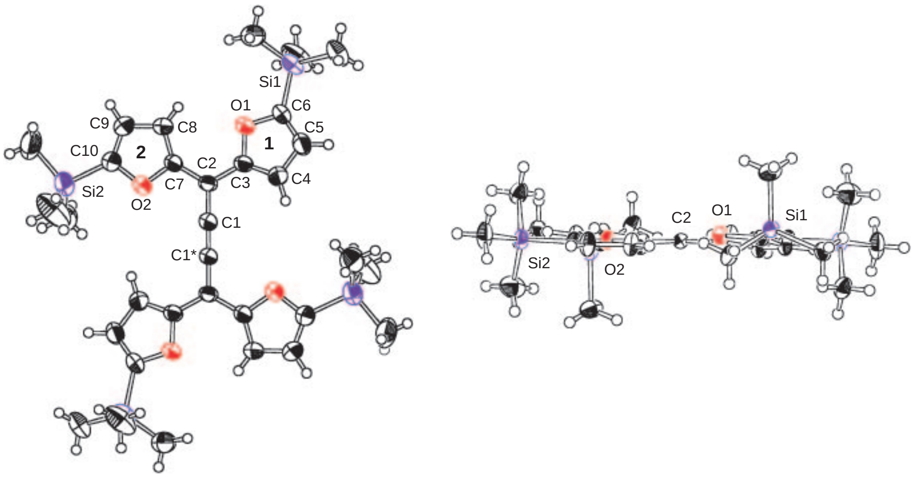


Fig. 2. ORTEP drawings of 1,1,4,4-tetrakis(5-trimethylsilyl-2-furyl)butatriene (**3b**) (50% thermal ellipsoids). Left: top view; right: view from C1–C2 axis.

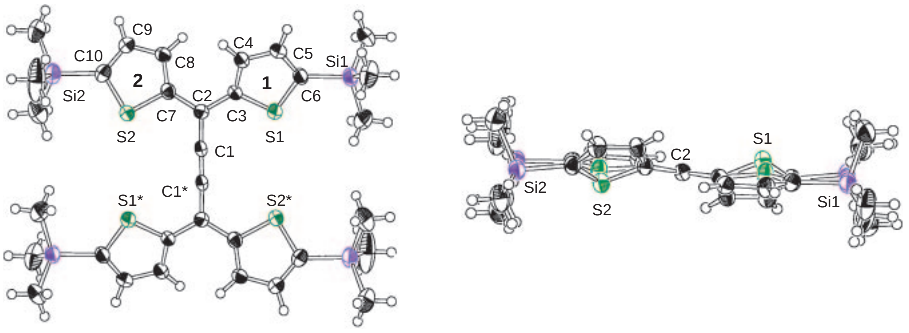


Fig. 3. ORTEP drawings of 1,1,4,4-tetrakis(5-trimethylsilyl-2-thienyl)butatriene (**4b**) (50% thermal ellipsoids). Left: top view; right: view from C1–C2 axis.

Table 3. Crystallographic Data for Tetrakis(trimethylsilylaryl)butatrienes (**3b**, **4b**, and **5b**)

	3b	**4b**	**5b**
Formula	$C_{32}H_{44}O_4Si_4$	$C_{32}H_{44}S_4Si_4$	$C_{32}H_{44}Se_4Si_4$
Formula weight	605.039	669.28	856.88
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Z	1	2	3
$a/\text{Å}$	8.2568(5)	8.9932(5)	12.325(1)
$b/\text{Å}$	10.2956(8)	18.113(1)	15.348(1)
$c/\text{Å}$	11.1063(9)	11.6300(5)	17.671(2)
$\alpha/°$	105.775(3)		105.551(2)
$\beta/°$	100.987(2)	99.5518(5)	107.989(3)
$\gamma/°$	93.042(2)		96.925(2)
$V/\text{Å}^3$	886.4(1)	1868.2(2)	2986.4(5)
$D_{\text{calcd}}/\text{g cm}^{-3}$	1.133	1.190	1.429
F_{000}	324.00	712.00	1284.00
$\mu(\text{Mo K}\alpha)/\text{cm}^{-1}$	1.99	4.03	38.17
No. of reflections	3416	15780	10536
$R1$	0.040	0.037	0.043
$wR2$	0.110	0.105	0.116
GOF	1.17	1.17	1.47

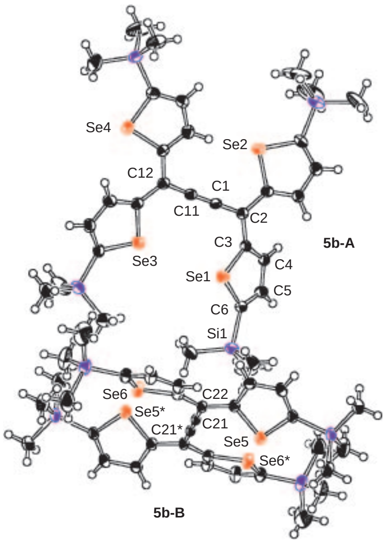


Fig. 4. ORTEP drawing of 1,1,4,4-tetrakis(5-trimethylsilyl-2-selenienyl)butatriene (**5b**) in a unit cell (50% thermal ellipsoids).

psuedo-D_2 symmetry in the crystals; the sulfur atoms of the aryl groups at each end of the molecule face each other (Fig. 3). The twist angles between planes of thiophenes and butatriene are 13.3° (ring 1) and 32.7° (ring 2). The distances between the sulfur atoms that face each other are 3.95 Å (S1$\cdots$S2*), which is longer than the van der Waals distance (3.70 Å).

The two conformers of **5b** are positioned in an edge-to-face

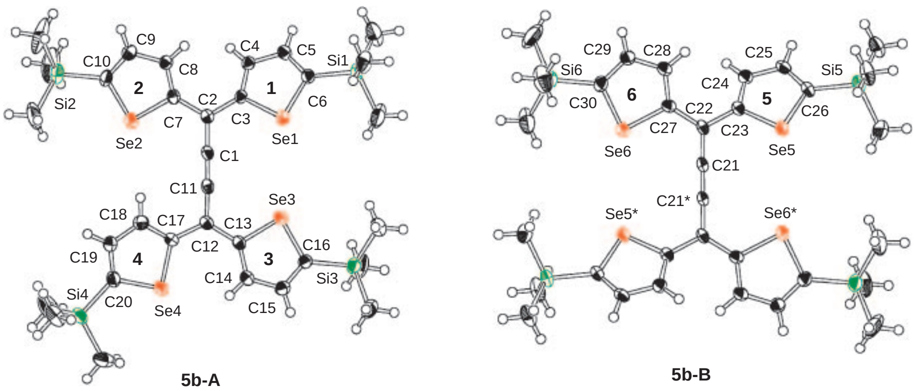


Fig. 5. The structures of the two conformers in the crystal of **5b**. Left: **5b-A**; right: **5b-B** (ORTEP drawings, 50% thermal ellipsoids).

Table 4. Selected Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°) for **3b**

C1–C1*	1.229(3)	C1–C2	1.360(2)
C2–C3	1.444(2)	C2–C7	1.446(2)
C3–C4	1.361(2)	C7–C8	1.359(2)
C4–C5	1.419(2)	C8–C9	1.418(2)
C5–C6	1.356(2)	C9–C10	1.353(2)
O1–C3	1.374(2)	O2–C7	1.367(2)
O1–C6	1.388(2)	O2–C10	1.393(2)
Si1–C6	1.866(2)	Si2–C10	1.866(2)
C1*–C1–C2	179.6(2)	C1–C2–C3	119.5(1)
C1–C2–C7	118.4(1)	C3–C2–C7	122.1(1)
O1–C3–C4	109.4(1)	C3–C4–C5	106.4(1)
C4–C5–C6	108.4(1)	O1–C6–C5	107.9(1)
C3–O1–C6	107.8(1)	O2–C7–C8	109.8(1)
C7–C8–C9	106.3(1)	C8–C9–C10	108.3(1)
O2–C10–C9	108.0(1)	C7–O2–C10	107.5(1)
C1–C2–C3–C4	−175.8(2)	C1–C2–C7–C8	10.7(3)
O1–C3–C2–C1	2.8(2)	O2–C7–C2–C1	−169.8(1)

Table 5. Selected Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°) for **4b**

C1–C1*	1.242(2)	C1–C2	1.353(1)
C2–C3	1.457(1)	C2–C7	1.470(1)
C3–C4	1.380(1)	C7–C8	1.367(1)
C4–C5	1.414(1)	C8–C9	1.416(1)
C5–C6	1.371(1)	C9–C10	1.375(1)
S1–C3	1.7274(8)	S2–C7	1.7280(9)
S1–C6	1.7329(9)	S2–C10	1.7237(8)
Si1–C6	1.8724(9)	Si2–C10	1.8712(9)
C1*–C1–C2	178.1(1)	C1–C2–C3	121.29(7)
C1–C2–C7	118.71(7)	C3–C2–C7	120.00(7)
S1–C3–C4	110.03(6)	C3–C4–C5	112.63(7)
C4–C5–C6	114.82(8)	S1–C6–C5	109.00(6)
C3–S1–C6	93.52(4)	S2–C7–C8	110.37(6)
C7–C8–C9	112.67(8)	C8–C9–C10	114.42(8)
S2–C10–C9	109.15(6)	C7–S2–C10	93.38(4)
C1–C2–C3–C4	−166.93(9)	C1–C2–C7–C8	−145.27(9)
S1–C3–C2–C1	12.7(1)	S2–C7–C2–C1	31.9(1)

manner (Fig. 4). One is non-symmetrical structure (**5b-A**); one of selenole rings faces in the opposite direction, while the other molecule has pseudo-D_2 symmetry (**5b-B**), as shown in Fig. 5. The twist-angles between planes of selenoles and butatriene are 26.2° (ring 1), 21.9° (ring 2), 13.7° (ring 3), 10.4° (ring 4), 35.7° (ring 5), and 12.0° (ring 6). The distance of the selenium atoms that face each other are 3.84 Å (Se1–Se3) and 3.97 Å (Se5–Se6*), which is slightly shorter than the van der Waals distance (4.00 Å).

These twist angles and distances between the heteroatoms that face each other probably reflect the counterbalance between the energy of conjugation and the repulsive nonbonded chalcogen–chalcogen interactions. The conformational differences in **3b–5b** can be understood by the fact that the C–S and C–Se bonds are considerably longer than the C–O bond.

The other structual feature of **3b–5b** is the short central double bonds (sp–sp) and long side double bonds (sp–sp^2). In Table 7, the central and side bond lengths of **3b–5b** together with the other known butatrienes (**1**, **18–25**) are summarized. Aryl-substituted butatrienes (**3b–5b**, **1**, **18**,[31] and **19**[32]) have shorter sp–sp bonds and longer sp–sp^2 bonds than those of alkyl-substituted and unsubstituted butatrienes (**20**[33] and **25**[34]) (Chart 4). Furthermore, a larger deviation in the bond lengths are observed in **3b–5b** than in **1**.

From the data, it appears that the conjugation between terminal substituents and a butatriene unit plays an important role in the deviation of bond lengths.[35] Furan derivative **3b**, a nearly planar butatriene, has the shortest sp–sp bond and the longest sp–sp^2 bond among the symmetrical butatrienes due to the effective conjugation along the four furyl rings and the butatriene skeleton. The relatively short sp–sp bond of **18** and **19** can be explained similarly. The two phenyl groups in **18** are nearly coplanar, and the four benzene rings connected to both ends of the triene in **19** are almost coplanar. Additionally, this conjugation effect is also applicable to the difference between tetrakis(trimethylsilyl) butatriene **21**[36] and tetrakis(trimethylsilylethynyl) derivative **22**[37] (1.276 Å vs 1.248 Å). The shortest value in the known butatrienes to date is 1.201 Å in 1,1-dicyano-4,4-bis(dimethylamino)butatriene (**23**).[38,39] This shortening is interpreted as the very high dipolar character of the push–pull butatriene. The *p*-quinopropadiene **24**,[40] recently prepared by us, also has a similar tendency. To verify fully our proposal, i.e., conjugation effects, detailed analytical studies of butatriene derivatives are required.

Table 6. Selected Bond Lengths (Å), Bond Angles (°), and Torsion Angles (°) for **5b**

Molecule **5b-A**			
C1–C2	1.357(4)		
C2–C3	1.456(5)	C2–C7	1.456(5)
C3–C4	1.378(4)	C7–C8	1.366(5)
C4–C5	1.414(6)	C8–C9	1.427(6)
C5–C6	1.372(5)	C9–C10	1.368(6)
Se1–C3	1.870(4)	Se2–C7	1.883(4)
Se1–C6	1.876(3)	Se2–C10	1.874(4)
Si1–C6	1.871(4)	Si2–C10	1.867(4)
C1–C11	1.240(4)	C11–C12	1.354(5)
C12–C13	1.453(6)	C12–C17	1.461(6)
C13–C14	1.363(5)	C17–C18	1.364(6)
C14–C15	1.408(7)	C18–C19	1.401(6)
C15–C16	1.356(5)	C19–C20	1.347(6)
Se3–C13	1.884(4)	Se4–C17	1.872(4)
Se3–C16	1.876(3)	Se4–C20	1.882(5)
Si3–C16	1.867(4)	Si4–C20	1.856(4)
C2–C1–C11	177.6(5)	C1–C2–C3	119.1(3)
C1–C2–C7	119.8(3)	C3–C2–C7	121.1(3)
Se1–C3–C4	110.1(3)	C3–C4–C5	114.8(3)
C4–C5–C6	117.5(3)	Se1–C6–C5	108.6(3)
C3–Se1–C6	89.0(2)	Se2–C7–C8	109.9(3)
C7–C8–C9	115.1(4)	C8–C9–C10	117.1(4)
Se2–C10–C9	109.0(3)	C7–Se2–C10	88.9(2)
C1–C11–C12	177.9(4)	C11–C12–C13	119.8(3)
C11–C12–C17	116.8(3)	C13–C12–C17	123.4(3)
Se3–C13–C14	109.0(3)	C13–C14–C15	115.9(3)
C14–C15–C16	117.5(3)	Se3–C16–C15	108.7(3)
C13–Se3–C16	88.8(2)	Se4–C17–C18	108.7(3)
C17–C18–C19	116.4(4)	C18–C19–C20	117.6(4)
Se4–C20–C19	108.4(3)	C17–Se4–C20	88.9(2)
C1–C2–C3–C4	152.2(5)	C1–C2–C7–C8	159.7(4)
Se1–C3–C2–C1	−26.2(6)	Se2–C7–C2–C1	−19.7(4)
C11–C12–C13–C14	165.3(5)	C11–C12–C17–C18	−10.8(6)
Se3–C13–C12–C11	−12.5(6)	Se4–C17–C12–C11	169.3(3)
Molecule **5b-B**			
C21–C21*	1.240(8)	C21–C22	1.353(6)
C22–C23	1.478(6)	C22–C27	1.457(4)
C23–C24	1.369(6)	C27–C28	1.367(5)
C24–C25	1.421(6)	C28–C29	1.412(5)
C25–C26	1.355(5)	C29–C30	1.364(7)
Se5–C23	1.866(4)	Se6–C27	1.873(4)
Se5–C26	1.881(4)	Se6–C30	1.877(4)
Si5–C26	1.860(4)	Si6–C30	1.865(4)
C21*–C21–C22	178.3(5)	C21–C22–C23	118.0(3)
C21–C22–C27	121.3(4)	C23–C22–C27	120.7(3)
Se5–C23–C24	110.6(3)	C23–C24–C25	114.5(3)
C24–C25–C26	117.4(4)	Se5–C26–C25	109.1(3)
C23–Se5–C26	88.4(2)	Se6–C27–C28	110.2(2)
C27–C28–C29	114.8(4)	C28–C29–C30	117.7(4)
Se6–C30–C29	108.6(2)	C27–Se6–C30	88.6(2)
C21–C22–C23–C24	143.2(4)	C21–C22–C27–C28	165.9(4)
Se5–C23–C22–C21	−33.7(5)	Se6–C27–C22–C21	−11.4(5)

Conclusion

The new butatrienes here presented are relatively stable crystalline substances with intense absorption in long wavelength region and considerably high redox properties. The poly-lithiated compounds derived from **4a**, **7a**, and **8a** are potential precursors for the novel extended π-electron systems.[41,42]

Experimental

General Methods. Melting points were recorded on a Yanaco MP 500D apparatus and are uncorrected. Mass spectral analyses (MS) were performed on a JEOL JMS-SX 102 and Shimadzu GCMS-QP5050A instrument. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-270 instrument. Chemical shifts are reported as δ referenced to Me_4Si. IR spectra were obtained on a Perkin-Elmer 1650 spectrometer. Microanalysis was performed at the Elemental Analysis Center, Faculty of Science, Osaka University. UV–vis spectra were obtained on a Hitachi U-3400 instrument. Cyclic voltammetry was performed on a Yanaco Model P-1000 cyclic voltammetric analyzer with a Yanaco Model FG-121B function generator. Column chromatography was performed with Merck Art. 7734 Kiesel-gel 60 and Merck Art. 1097 Aluminum Oxide 90.

Materials. Di(2-furyl)methanone (**9a**)[43] and di(2-thienyl)methanone (**10a**)[44] were prepared from reported procedures. Di(2-selenienyl)methanone (**11a**)[45] was synthesized similar to **9a**. 2-Trimethylsilylfuran was prepared according to the literature.[46] All solvents were dried by using conventional procedures.

Bis(5-trimethylsilyl-2-furyl)methanone (9b). To a stirred solution of 2-trimethylsilylfuran (1.41 g, 10.0 mmol) in anhydrous tetrahydrofuran (18 mL) was added *n*-BuLi (8.0 mL, 12.0 mmol) at 0 °C under a nitrogen atmosphere. After stirring at room temperature for 4 h, dimethylcarbamoyl chloride (0.5 mL, 5.4 mmol) was added dropwise at 0 °C, and then, the mixture was stirred at room temperature for 2 h. The reaction was quenched with a saturated aqueous solution of NH_4Cl (10 mL), and the aqueous layer was extracted with ether. The organic layer was washed with brine, and dried over anhydrous Na_2SO_4, and the solvent was evaporated. The residue was chromatographed on silica gel (50 g) using hexane–ethyl acetate (80:20) as eluent to give **9b** (1.00 g, 65%) as a colorless oil. Recrystallization from hexane in a refrigerator gave colorless needles.

9b: colorless needles; mp 52–53 °C; MS (EI) *m/z* 306 (M^+, 100), 291 [$(M - CH_3)^+$, 84]; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.35 (s, 18H), 6.76 (d, $J = 3.7$ Hz, 2H), 7.48 (d, $J = 3.7$ Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −1.64, 119.11, 121.31, 155.38, 166.42, 168.77; Found: C, 58.53; H, 7.17%; Calcd for $C_{15}H_{22}O_3Si_2$: C, 58.78, H, 7.23%.

1,1-Dichloro-2,2-di(2-thienyl)ethene (7a). General Procedure for Preparation of Dichloroethenes. A solution of di(2-thienyl)methanone (**10a**) (22 g, 113.2 mmol) and triphenylphosphine (118.8 g, 453 mmol) in carbon tetrachloride (400 mL) was heated at reflux for 18 h under a nitrogen atmosphere with vigorous stirring. The resulting suspension was cooled and decanted. The residue was washed with benzene (50 mL × 2). The combined organic solution was concentrated under reduced pressure. The solution was then diluted with CH_2Cl_2 (50 mL) and hexane (300 mL). The white solid that formed was removed by filtration, and the filtrate was evaporated. The residue was chromatographed on silica gel. The hexane eluent was evaporated to give a yellow

Table 7. The sp–sp and sp–sp^2 Bond Lengths in Butatriene Derivatives (Å)

Compound	sp–sp	sp–sp^2	Ref.	Compound	sp–sp	sp–sp^2	Ref.
3b	1.229(3)	1.360(2)	this work	**20**	1.261	1.332	33
4b	1.242(2)	1.353(1)	this work	**21**	1.276(8)	1.319(6)	36
5b-A	1.240(4)	1.354(5) 1.357(4)	this work	**22**	1.248(1)	1.353(1)	37
5b-B	1.240(8)	1.353(6)					
1	1.260(2)[a)]	1.346(2)[a)] 1.349(2)[a)]	11	**23**	1.201(2)	1.377(2) 1.397(2)	38,39
18	1.253(3)	1.322(3) 1.333(3)	31	**24**	1.228(5)	1.356(5) 1.380(5)	40
19	1.24(1)	1.341(7)	32	**25**	1.283(5)[b)]	1.318(5)[b)]	34

a) Data measured at −160 °C. b) Data measured by electron diffraction.

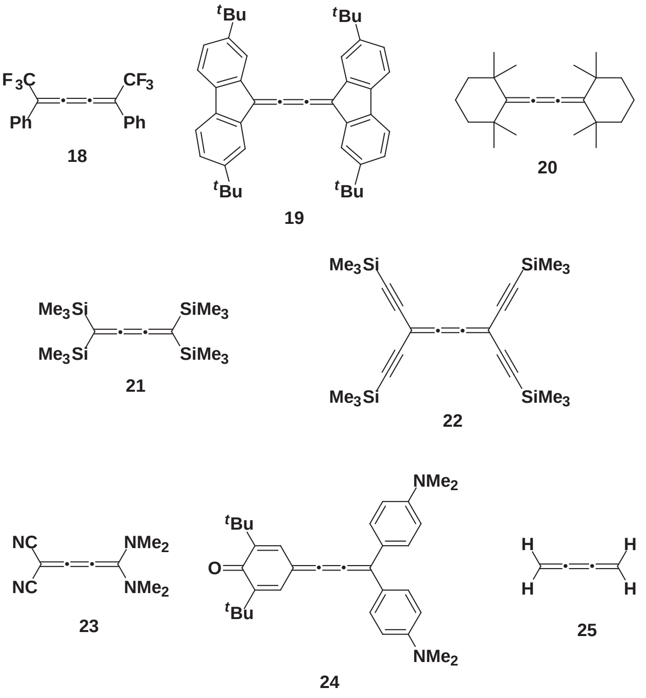


Chart 4.

residue, which was distilled under reduced pressure to give **7a** (23.9 g, 85%). The procedure also gave **6a** (88%) from **9a**, **6b** (86%) from **9b**, and **8a** (94%) from **11a**.

7a: pale yellow oil; bp 138–140 °C/6 mmHg (lit.[22] 102 °C/0.5 mmHg); MS (EI) m/z 260 $[M^+(^{35}Cl \times 2), 19]$, 190 $[(M - Cl_2)^+, 100]$; ^1H NMR (270 MHz, $CDCl_3$) δ 7.02 (dd, $J = 3.6$, 5.0 Hz, 2H), 7.06 (dd, $J = 1.5$, 3.6 Hz, 2H), 7.40 (dd, $J = 1.5$, 5.0 Hz, 2H).

1,1-Dichloro-2,2-di(2-furyl)ethene (6a): Colorless oil; bp 105–107 °C/7 mmHg; MS (EI) m/z 230 $[M^+(^{37}Cl, ^{35}Cl), 55]$, 228 $[M^+(^{35}Cl \times 2), 100]$, 165 (56); ^1H NMR (270 MHz, $CDCl_3$) δ 6.47 (dd, $J = 2.0$, 3.3 Hz, 2H), 6.58 (dd, $J = 1.6$, 3.3 Hz, 2H), 7.47 (dd, $J = 1.6$, 2.0 Hz, 2H); HRMS Found: m/z 227.9740. Calcd for $C_{10}H_6Cl_2O_2$: $[M]^+$, 227.9735.

1,1-Dichloro-2,2-bis(5-trimethylsilyl-2-furyl)ethene (6b): Pale yellow crystals; mp 44–46 °C; MS (EI) m/z 376 $[M^+(^{37}Cl \times 2), 13]$, 374 $[M^+(^{37}Cl, ^{35}Cl), 72]$, 372 $[M^+(^{35}Cl \times 2), 100]$, 357 (13); ^1H NMR (270 MHz, $CDCl_3$) δ 0.27 (s, 18H), 6.48 (d, $J = 3.3$ Hz, 2H), 6.66 (d, $J = 3.3$ Hz, 2H); HRMS Found: m/z 372.0527. Calcd for $C_{16}H_{22}Cl_2O_2Si_2$: $[M]^+$, 372.0535.

1,1-Dichloro-2,2-di(2-selenienyl)ethene (8a): Colorless oil; bp 175 °C/1 mmHg; MS (EI) m/z 356 $[M^+(^{80}Se, ^{35}Cl), 100]$, 319 (29), 285 (68), 225 (45), 205 (38); ^1H NMR (270 MHz, $CDCl_3$) δ 7.21 (dd, $J = 1.3$, 4.0 Hz, 2H), 7.25 (dd, $J = 3.3$, 5.3 Hz, 2H), 8.12 (dd, $J = 1.3$, 5.3 Hz, 2H); HRMS Found: m/z 355.8193. Calcd for $C_{10}H_6Cl_2Se_2$: $[M]^+$, 355.8184.

1,1-Dichloro-2,2-bis(5-trimethylsilyl-2-thienyl)ethene (7b). General Procedure for Difunctionalization of 7a. To a solution of lithium diisopropylamide, prepared by the reaction of diisopropylamine (1.7 mL, 12 mmol) and n-BuLi (5.6 mL, 9 mmol) in THF (20 mL), was added a solution of **7a** (783 mg, 3 mmol) in THF (5 mL) at −50 °C under a nitrogen atmosphere. The reaction mixture was allowed to warm to 0 °C in an ice bath and stirred for 30 min. After cooling at −50 °C, chlorotrimethylsilane (1.2 mL, 10 mmol) was added. After stirring for an additional 10 min, the reaction mixture was allowed to warm to 0 °C and stirred for 20 min. Then, water (30 mL) and hexane (20 mL) were added to the mixture. The organic layer was separated, washed with brine, and dried over anhydrous $MgSO_4$, and the solvent was evaporated. The residue was chromatographed on silica gel (10 g) using hexane to hexane–benzene (95:5) as eluent to give bis(trimethylsilyl) derivative **7b** (1.16 g, 95%).

Upon quenching with dimethyl disulfide, bismethylthio derivative **7c** (53%) was obtained from of **7a**, and upon quenching with chlorotrimethylsilane, bis(trimethylsilyl) derivative **8b** (85%) was obtained from **8a**.

7b: Pale yellow crystals; mp 77–78 °C; MS (EI) m/z 408 $[M^+(^{37}Cl \times 2), 25]$, 406 $[M^+(^{37}Cl, ^{35}Cl), 69]$, 404 $[M^+(^{35}Cl), 92]$, 393 $[(M - CH_3)^+(^{37}Cl \times 2), 26]$, 391 $[(M - CH_3)^+(^{37}Cl, ^{35}Cl), 79]$, 389 $[(M - CH_3)^+(^{35}Cl \times 2), 100]$; ^1H NMR (270 MHz, $CDCl_3$) δ 0.34 (s, 18H), 7.08 (d, $J = 3.6$ Hz, 2H), 7.14 (d, $J = 3.6$ Hz, 2H); Found: C, 47.24; H, 5.33%. Calcd for $C_{16}H_{22}Cl_2S_2Si_2$: C, 47.38, H, 5.48%.

1,1-Dichloro-2,2-bis(5-methylthio-2-thienyl)ethene (7c): Pale yellow oil; MS (EI) m/z 356 $[M^+(^{37}Cl \times 2), 23]$, 354 $[M^+(^{37}Cl, ^{35}Cl)$ 83,], 352 $[M^+(^{35}Cl \times 2)$ 100,]; ^1H MNR (270 MHz, $CDCl_3$) δ 2.52 (s, 6H), 6.87 (d, $J = 3.8$ Hz, 2H), 6.94 (d, $J = 3.8$ Hz, 2H).

1,1-Dichloro-2,2-bis(5-trimethylsilyl-2-selenienyl)ethene (8b): Colorless needles; mp 103–104 °C; MS (FAB) m/z 502 (M^+); ^1H NMR (270 MHz, $CDCl_3$) δ 0.32 (s, 18H), 7.24 (d, $J = 3.7$ Hz, 2H), 7.40 (d, $J = 3.7$ Hz, 2H); Found: C, 38.47; H, 4.56%. Calcd for $C_{16}H_{22}Cl_2Se_2Si_2$: C, 38.48; H, 4.44%.

General Procedure for the Synthesis of Butatrienes. To a solution of **7a** (2.0 mmol) in THF (5 mL) was added n-BuLi (1.25 mL, 2 mmol) at −90 °C under a nitrogen atmosphere. After stirring at that temperature for 1 h, well-dried CuCN (90 mg, 1.0 mmol) was added to the mixture all at once. After an additional 1 h of stirring, the mixture was allowed to warm to rt, and stirred for 10 h. To the resulting reddish purple solution was added water (30 mL) and hexane (10 mL). The organic layer was separated, washed with brine, and dried over anhydrous $MgSO_4$, and the solvent was evaporated. The residue was chromatographed on silica gel (20 g) using hexane–benzene (95:5–80:20) as eluent to give **4a** (196 mg, 51%). The procedure also gave **3a** (99 mg, 50%) from 1.2 mmol of **6a**, **3b** (371 mg, 61%) from **6b**, **4b** (433 mg, 65%) from **7b**, **4c** (203 mg, 40%) from **7c**, and **5b** (264 mg, 64%) from **8b**. In the case of **6b**, hexakis(5-trimethylsilyl-2-furyl)[3]radialene **12** (13 mg, 2%) was obtained as a by-product.

1,1,4,4-Tetra(2-furyl)butatriene (3a): Reddish needles; mp 128–132 °C (decomp); MS (EI) m/z 316 (M^+, 100), 287 (7), 231 (11), 202 (36); ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.55 (dd, $J = 1.7$, 3.6 Hz, 4H), 6.97 (br d, $J = 3.5$ Hz, 4H), 7.57 (br d, $J = 3.5$ Hz, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 100.59, 111.63, 112.49, 136.30, 143.39, 150.94; IR (KBr) ν 3116m, 2926m, 1723w, 1618w, 1529m, 1476s, 1377m, 1307m, 1226s, 1155s, 1074s, 1025s, 969s, 913m, 883s, 831s, 800s, 726s, 593s cm^{-1}; UV–vis $\lambda_{\max}$ (CH_2Cl_2) 501 ($\log \varepsilon$ 4.73), 382 (3.93), 289 (4.51) nm; Found: C, 75.90; H, 3.85%. Calcd for $C_{20}H_{12}O_4$: C, 75.94; H, 3.83%.

1,1,4,4-Tetrakis(5-trimethylsilyl-2-furyl)butatriene (3b): Deep red needles; mp 191–192 °C; MS (FAB) m/z 605 [$(M+1)^+$, 19], 604 (M^+, 30), 154 (100); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.36 (s, 36H), 6.77 (d, $J = 3.3$ Hz, 4H), 7.06 (d, $J = 3.3$ Hz, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −1.41, 100.76, 111.93, 122.19, 135.09, 155.33, 161.89; IR (KBr) 2956m, 1552w, 1335w, 1249s, 1188m, 1112s, 1026m, 931s, 834s, 792s, 755s, 627m cm^{-1}; UV–vis $\lambda_{\max}$ (CH_2Cl_2) 545 ($\log \varepsilon$ 4.80), 403 (4.01), 319 (4.54), 306 (4.59) nm; Found: C, 63.67; H, 7.36%. Calcd for $C_{32}H_{44}O_4Si_4$: C, 63.51; H, 7.34%.

1,1,4,4-Tetra(2-thienyl)butatriene (4a): Red prisms; mp 199–200 °C; MS (EI) m/z 380 (M^+); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.11 (dd, $J = 3.6$, 5.3 Hz, 4H), 7.40 (dd, $J = 1.0$, 5.3 Hz, 4H), 7.51 (dd, $J = 1.0$, 3.6 Hz, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 108.95, 127.35, 127.62, 127.93, 140.53, 142.59; IR (KBr) ν 3098m, 2904s, 1666m, 1416s, 1363m, 1339m, 1274m, 1215m, 1111w, 1078m, 1040m, 850s, 832s, 807m, 770s, 700s, 627m, 606w cm^{-1}; UV–vis $\lambda_{\max}$ (CH_2Cl_2) 501 ($\log \varepsilon$ 4.54), 312 (4.40) nm; Found: C, 63.05; H, 3.15%. Calcd for $C_{20}H_{12}S_4$: C, 63.11; H, 3.18%.

1,1,4,4-Tetrakis(5-trimethylsilyl-2-thienyl)butatriene (4b): Red prisms; mp 155–156 °C; MS (EI) m/z 668 (M^+); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.25 (s, 36H), 7.12 (d, $J = 3.5$ Hz, 4H), 7.45 (d, $J = 3.5$ Hz, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −0.07, 108.91, 128.70, 134.67, 139.90, 143.12, 147.81; IR (KBr) ν 3060w, 2955m, 1568w, 1499w, 1404w, 1289w, 1250s, 1198m, 1065s, 988s, 836s, 802s, 756s, 695w, 631m cm^{-1}; UV–vis $\lambda_{\max}$ (CH_2Cl_2) 530 ($\log \varepsilon$ 4.79), 337 (4.79), 326 (4.75) nm; Found: C, 57.28; H, 6.57%. Calcd for $C_{32}H_{44}S_4Si_4$: C, 57.42; H, 6.64%.

1,1,4,4-Tetrakis(5-methylthio-2-thienyl)butatriene (4c): Reddish purple prisms; mp 160 °C (decomp); MS (FAB) m/z 564 (M^+); ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.09 (s, 12H), 6.80 (d, $J = 3.7$ Hz, 4H), 7.25 (d, $J = 3.7$ Hz, 4H); ^{13}C NMR (67.8 MHz, C_6D_6) δ 20.74, 108.50, 130.58, 138.89, 141.25, 143.68; UV–vis $\lambda_{\max}$ (CH_2Cl_2) 562 ($\log \varepsilon$ 4.59), 358 (4.51) nm; Found: C, 50.85; H, 3.57%. Calcd for $C_{24}H_{20}S_8$: C, 51.02; H, 3.59%.

1,1,4,4-Tetrakis(5-trimethylsilyl-2-selenienyl)butatriene (5b): Reddish purple prisms; mp 162–163 °C; MS (FAB) m/z 860 (M^+); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.36 (s, 36H), 7.55 (d, $J = 4.0$ Hz, 4H), 7.75 (d, $J = 4.0$ Hz, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −0.24, 113.25, 130.24, 136.70, 138.41, 151.50, 152.79; IR (KBr) ν 2914w, 1565m, 1488w, 1414s, 1299m, 1110m, 1064m, 1007m, 961m, 781s, 622m cm^{-1}; UV–vis $\lambda_{\max}$ (CH_2Cl_2) 552 ($\log \varepsilon$ 4.68), 350 (4.66), 340 (4.66) nm; Found: C, 44.96; H, 5.24%. Calcd for $C_{32}H_{44}Se_4Si_4$: C, 44.85: H, 5.19%.

Hexakis(5-trimethylsilyl-2-furyl)[3]radialene (12): Blue-green crystals; mp 192–193 °C; MS (FAB) m/z 906 (M^+); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.18 (s, 54H), 6.07 (d, $J = 3.3$ Hz, 6H), 6.48 (d, $J = 3.3$ Hz, 6H), ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −1.38, 102.07, 113.77, 116.86, 121.62, 156.36, 161.01; UV–vis $\lambda_{\max}$ (CH_2Cl_2) 633 ($\log \varepsilon$ 4.25), 426 (4.21), 290 (4.52), 227 (4.59) nm.

Lithiation of 1,1,4,4-Tetra(2-thienyl)butatriene (4a). To a solution of LDA (5.0 mmol), prepared by reacting diisopropylamine (0.7 mL, 5.3 mmol) and n-BuLi (3.1 mL, 5.0 mmol) in THF (10 mL) under a nitrogen atmosphere, was added **4a** (380 mg, 1 mmol) at −78 °C. The reaction mixture was allowed to warm to 0 °C for 30 min with stirring, and then cooled at −78 °C. Chlorotrimethylsilane (1 mL, 7.9 mmol) was added via syringe. After 30 min with stirring at −78 °C, the reaction mixture was allowed to warm to rt and was quenched with water (20 mL). Hexane–benzene (1:1, 100 mL) was added to the mixture. The organic layer was separated, washed with brine, and dried over anhydrous $MgSO_4$, and the solvent was evaporated. The residue was chromatographed on silica gel (10 g) using hexane as eluent to give 174 mg of **4b** (26%).

X-ray Analysis. Single crystals of **3b**, **4b**, and **5b** were grown by the slow evaporation of saturated solutions in hexane. The diffraction data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) to a maximum 2θ value of 55.0° at 150 K. The structure was solved by direct methods (SIR92[47]) and refined by the full-matrix least-squares method by using teXsan crystallographic software package of Molecular Structure Corporation.[48] Anisotropic thermal parameters were employed for non-hydrogen atoms, and all hydrogens were located by calculation. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition number CCDC-619571 for **3b**, 619572 for **4b**, and 619573 for **5b**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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