NEW SYNTHESES OF TRICYCLIC THIOPHENES AND CYCLIC TETRATHIOPHENES USING TRANSITION-METAL-CATALYZED CYCLIZATION

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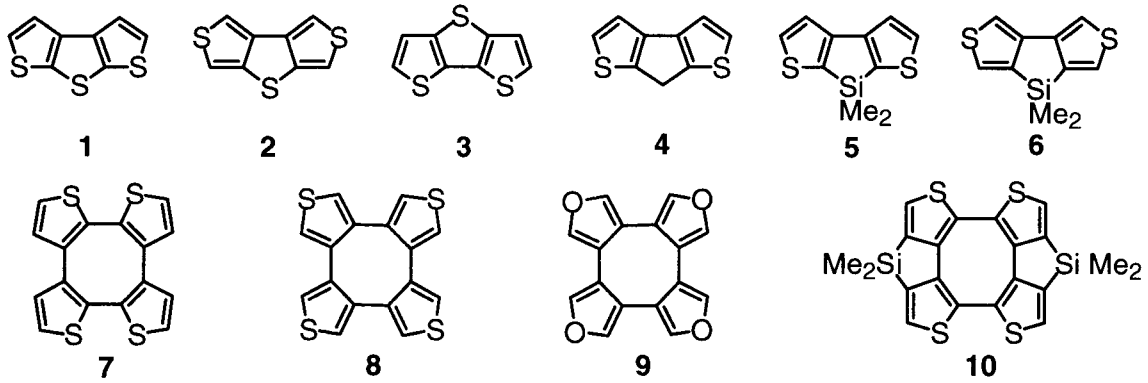
Abstract- New synthetic methods for polycyclic thiophenes were developed. Thus, dithienothiophenes, cyclopentadithiophene, silacyclopentadithiophenes, and cyclooctatetrathiophenes were synthesized in moderate to good yields by using the $CuCl_2$-mediated cyclization of organocopper(I) and organozinc intermediates prepared from dilithio-derivatives with CuCN or $ZnCl_2$, respectively. A direct cyclization of bromothiophene derivatives with hexamethylditin in the presence of tetrakis(triphenylphosphine)palladium(0) also gave dithienothiophenes, cyclopenta-dithiophenes, and silacyclopentadithiophenes in good yields.

Introduction

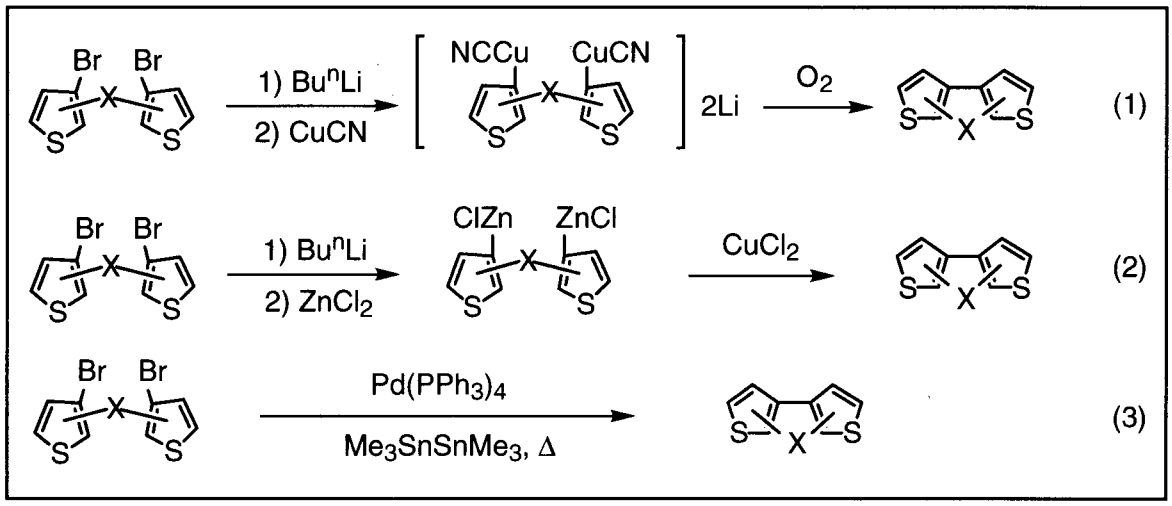
Dithienothiophenes (**1**, **2** and **3**), cyclooctatetrathiophenes (**7** and **8**), and related compounds (**4**-**6** and **9**-**10**) have received considerable attention, because dithienothiophenes possess three different types of π-conjugation which plays an important role as a spacer and donor,[1-4] and because these polycyclic compounds give conjugated polymers with unique features.[5] Although [3,2-*b*: 2',3'-*d*]dithienothiophene[6] (**3**) can be easily prepared and has been employed frequently as the spacer and donor, the synthetic inconvenience of [2,3-*b*:3',2'-*d*]- and [3,4-*b*:3',4'-*d*]dithienothiophenes (**1** and **2**) and related compounds (**4**-**10**)[7,8] has prevented the use of these compounds as building blocks for organic synthesis. We report



1 **2** **3** **4** **5** **6**

7 **8** **9** **10**

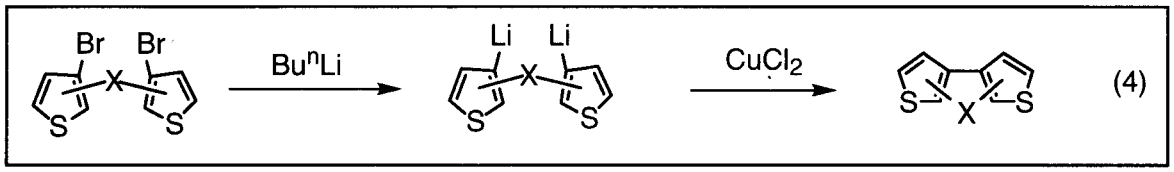
here a convenient method for the synthesis of dithienothiophenes, cyclopentadithiophene and silacyclopentadithiophenes (**1**, **2**, and **4**- **6**), together with cyclooctatetrathiophenes and cyclooctatetrafuran (**7**-**10**). As shown in eqs. 1-3, we developed three new methods for the synthesis of polycyclic thiophenes and their derivatives. The first one is the coupling of ate-type copper(I) complexes with molecular oxygen (eq. 1).[9] The second one is the copper-catalyzed intramolecular coupling of organozinc derivatives (eq. 2).[10] The third one is the cyclization of bromothiophene derivatives with hexamethylditin in the presence of tetrakis(triphenylphosphine)palladium(0) (eq. 3).[11,12] We reported in preliminary form the palladium-catalyzed cyclization of bromothiophenes to produce polycyclic thiophenes in good yields.[12] In this paper we detail the successful execution of eqs. 1-3, together with some related reactions.



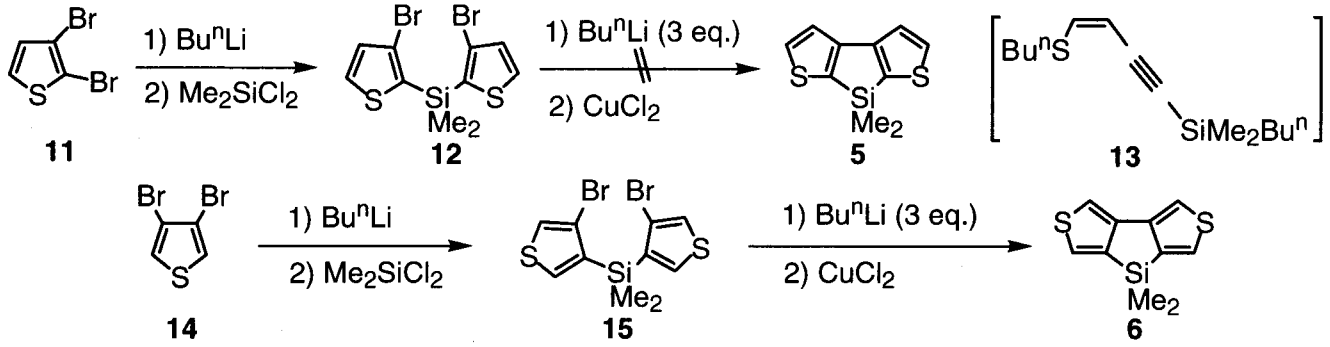
Results and Discussion

Cyclization of Ate-Type Copper Complexes (Method 1).

The carbon-carbon coupling reaction using lithiation, followed by $CuCl_2$-oxidation is a useful method for the synthesis of polycyclic arenes and heteroarenes.[8] Thus, dithienothiophenes (**1**-**3**) and cyclopentadithiophene (**4**) can be synthesized by using this $CuCl_2$-catalyzed coupling reaction (eq. 4).[6,7] Therefore, we first applied this method to the synthesis of silacyclopentadithiophenes (**5** and **6**)[12] (Scheme 1).



Although the successive treatments of **15** with 2.2 equiv. of Bu^{n}Li and 3.0 equiv. of $CuCl_2$ produced the desired coupling product (**6**) in 30% yield, a similar reaction of **12** gave a complex mixture containing no cyclized product (**5**), and only the compound (**13**)[13] was isolated in 9% yield (Scheme 1). We surprised at these results and reexamined the copper-catalyzed cyclizations under various conditions.



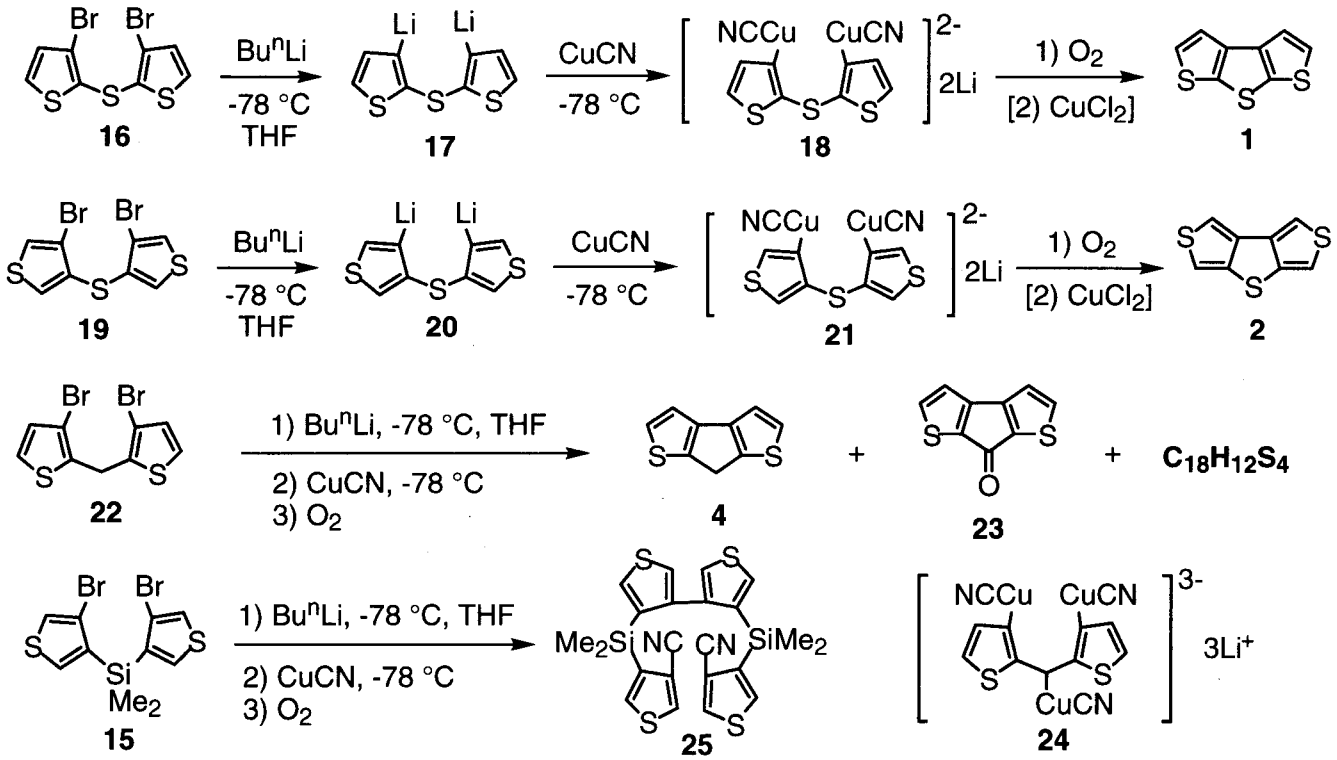
Scheme 1

The carbon-carbon coupling reaction using oxidation of ate-type copper complexes with molecular oxygen was employed recently for the synthesis of polycyclic arenes,[14] although this type of reaction was reported in the initial studies on the reactivity of ate-type copper complexes.[15] Therefore, we examined the cyclization reaction of an ate-type copper complex using O_2-oxidation as outlined in eq. 1. As shown in Scheme 2 and Table 1, the dibromodithiophenes (**16** and **19**) were treated with Bu^{n}Li (2.2 equiv.) at -78 °C to yield dilithiated intermediates which were treated with CuCN (2.5 equiv.) to produce the corresponding mixed cuprates (**18** and **21**). The oxidation of **18** and **21** with molecular oxygen at -78 °C to room temperature produced the dithienothiophenes (**1** and **2**) in 37 and 40% yields, respectively (entries 1 and 4). The reaction needed fairly diluted conditions (1 mmol of **1** or **2** in 60 ml of THF), and more concentrated conditions (1 mmol of **1** or **2** in 10 ml of THF) gave lower yields of products (entries 2 and 5). Interestingly, successive treatments of **18** and **21** with O_2 at -78 °C and $CuCl_2$ (3 equiv.) at -78 °C to room temperature produced **1** and **2** in 47 and 49% yields, respectively (entries 3 and 6). In a similar manner, the reaction of **22** with Bu^{n}Li (2.2 equiv.), followed by treatment with CuCN (2.5 equiv.) and O_2 resulted in the formation of **4** in 40% yield, together with the ketone (**23**)[16] and a dimeric compound ($C_{18}H_{12}S_4$) in 5 and 3% yields, respectively (entry 7). The yield of **23** was increased to 25%, when excess amounts of Bu^{n}Li (4.5 equiv.) and CuCN (6 equiv.) were employed. This result suggests that the mixed cuprate (**24**) may lead to the formation of **23** *via* O_2-oxidation. In contrast, a similar reaction of **15** led to the acyclic dimer (**25**) in 9% yield, together with unidentified by-products.

Table 1. Cyclizations of the dibromides (**15-16, 19** and **22**).[a]

entry	Compound	Procedure	THF (ml)[b]	Product	Yield/%
1	**16**	A	60	**1**	37
2	**16**	A	10	**1**	22
3	**16**	B	60	**1**	47
4	**19**	A	60	**2**	40
5	**19**	A	10	**2**	14
6	**19**	B	60	**2**	49
7	**22**	A	60	**4**	40[c]

[a]Conditions. Procedure A: 1) Bu^{n}Li (2.2 equiv.), 2) CuCN (2.5 equiv.), 3) O_2 (excess). Procedure B: 1) Bu^{n}Li (2.2 equiv.), 2) CuCN (2.5 equiv.), 3) O_2 (excess), 4) $CuCl_2$ (3.0 equiv.). [b]Total volume of solvents used. [c]The ketone (**23**) (5%) and dimer (3%) were also isolated.



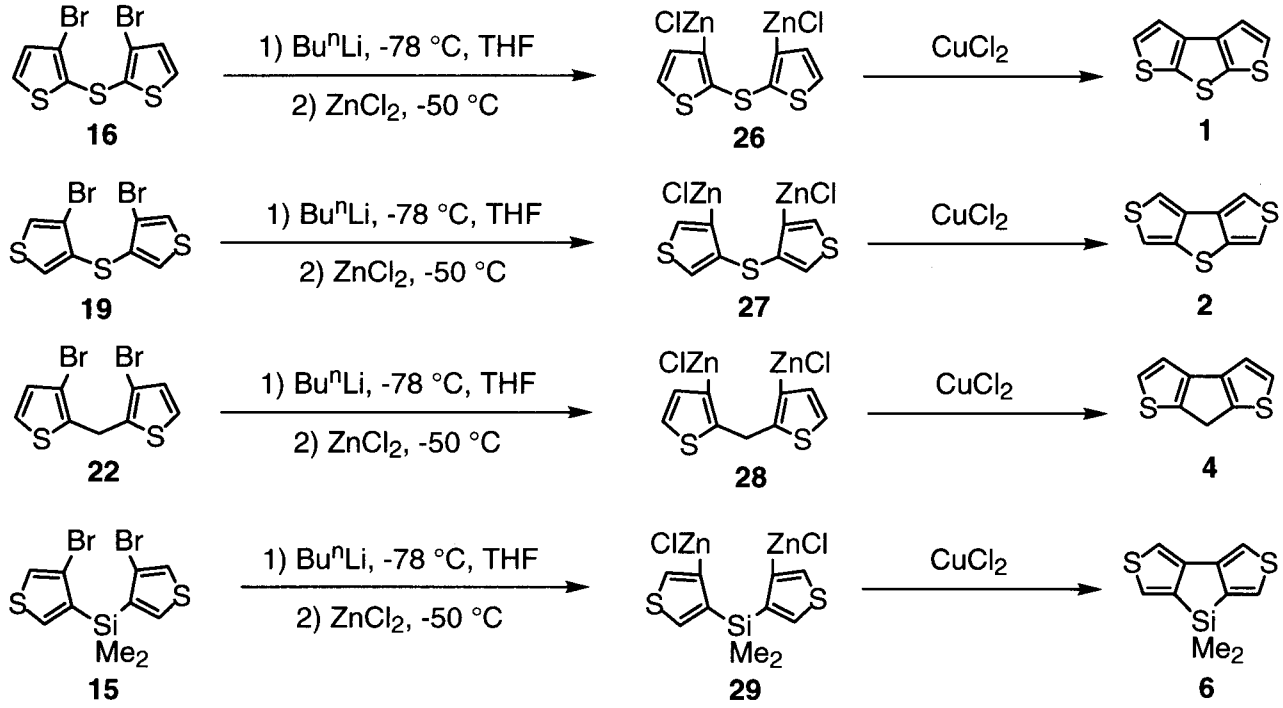
Scheme 2

The molecular structure of the unusual product (**25**) was determined by X-Ray analysis (see EXPERIMENTAL). Although the reactions of mixed cuprates derived from CuCN have been investigated widely,[15,17] to our knowledge, this is the first example of the unusual cross-coupling reaction between sp^2- and nitrile-sp carbons of ligands attached to ate-type copper complexes.

Cyclization of Organozinc Species with $CuCl_2$ (Method 2).

Recently, we have found that diarylzinc species react with $CuCl_2$ smoothly to produce the corresponding homo-coupling products in good yields, and this reaction has been applied to the synthesis of biphenylenes.[18] Since the biphenylene synthesis *via* the organozinc species can be achieved in better yield as compared with the cyclization of the organolithium species, we applied this method to the synthesis of polycyclic thiophenes (eq. 2).

As shown in Scheme 3, the dibromides (**16**, **19**, **22**, and **15**), when treated successively with Bu^{n}Li, $ZnCl_2$ and $CuCl_2$, produced the corresponding coupling products (**1**, **2**, **4**, and **6**) in good yields. As summarized in Table 2, the dibromides (**16**, **19**, **22**, and **15**) reacted with Bu^{n}Li (2.2 equiv.) at -78 °C to afford the corresponding dilithio intermediates which were treated with $ZnCl_2$ (2.4 mmol) at -50 °C to produce the arylzinc intermediates (**26**, **27**, **28**, and **29**), followed by oxidation with $CuCl_2$ (3 equiv.) at -78 °C to give the corresponding cyclized products (**1**, **2**, **4**, and **6**) in 69, 70, 55, and 61% yields, respectively (entries 1, 3, 5, and 7). In a similar manner to the coupling of ate-type complexes, cyclization of the zinc species (**26-29**) proceeded smoothly only in dilute conditions (1 mmol of **16**, **19**, **22** or **15** in 60 mL of THF), and normal conditions (1 mmol of substrate in 15 mL of THF) produced lower yields of products (entries 2, 4, 6, and 8).



Scheme 3

Table 2. Cyclizations of the dibromides (**15-16, 19** and **22**).[a]

entry	Compound	THF (ml)[b]	Product	Yield/%
1	**16**	60	**1**	69
2	**16**	15	**1**	45
3	**19**	60	**2**	70
4	**19**	15	**2**	49
5	**22**	60	**4**	55
6	**22**	15	**4**	51
7	**15**	60	**6**	61
8	**15**	15	**6**	40

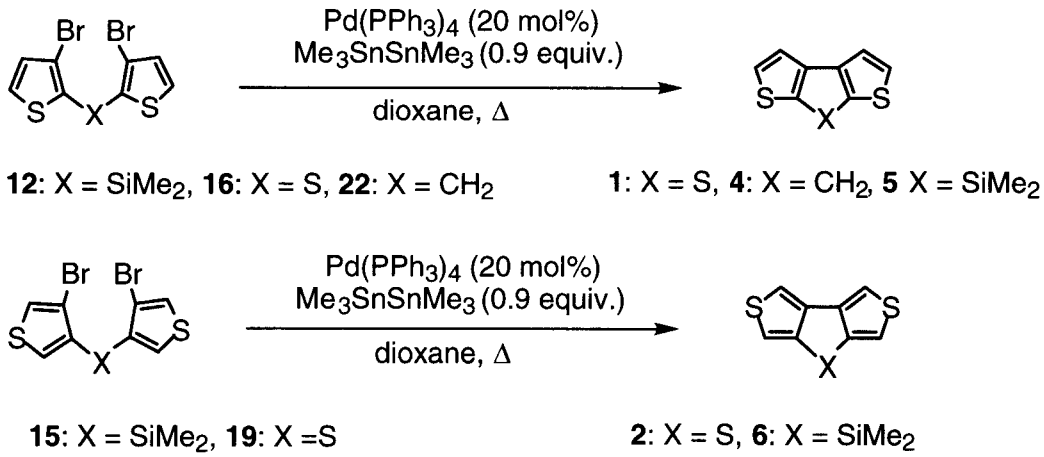
[a]Conditions: 1) Bu^{n}Li (2.2 equiv.), 2) $ZnCl_2$ (2.4 equiv.), 3) $CuCl_2$ (3 equiv.). [b]Total volume of THF used for the reaction.

As shown in Table 2, the cyclization of organozinc species with $CuCl_2$ proceeded smoothly under diluted conditions to produce polycyclic thiophenes in good yields. Although the coupling reactions of the organolithium species with $CuCl_2$ have been used frequently for the synthesis of polycyclic thiophenes,[6] our method using the coupling of organozinc intermediates can be widely employed for the synthesis of polycyclic thiophenes. The improvement of the yields of the coupling products may depend on the facility in transmetallation. The easier transmetallation[19] from zinc(II) to copper(II) compared to that from lithium(I) to copper(II) leads to better yields of the coupling products (**1**, **2**, **4** and **6**).

Palladium-Catalyzed Cyclization of Dibromodithiophenes (Method 3).

Recently, palladium-catalyzed coupling reactions are recognized as one of the most useful methods for the carbon-carbon bond formation. Thus, numerous reports have appeared which showed the effectiveness of

palladium-catalyzed coupling and cross-coupling reactions.[20] We applied the palladium-catalyzed cyclization of dibromodithiophenes (**16**, **19**, **22**, **12**, and **15**) to the synthesis of **1**, **2** and **4-6**. The new method for the synthesis of dithienothiophenes and related compounds using $Pd(PPh_3)_4$ catalysts is outlined in Scheme 4 and Table 3. The palladium-catalyzed cyclization of **16** was first carried out using 15 mol% of $Pd(PPh_3)_4$ and 0.9 equiv. of hexamethylditin in dioxane at 110 °C for 24 h to produce **1** in 55% yield, but 38% of **16** was recovered in this case (entry 1).[21] A similar reaction using 15 mol% of $Pd(PPh_3)_4$ and 0.5 equiv. of PPh_3 gave the product (**1**) in 67% yield, together with a small amount



Scheme 4

Table 3. Palladium-catalyzed cyclizations.[a]

entry	Compound	$Pd(PPh_3)_4$/mol%	Temp./C	Time/h	Product	Yield %
1	**16**	15[b]	110	24	**1**	55[c]
2	**16**	15	160	24	**1**	67[c]
3	**16**	20	160	24	**1**	75
4	**19**	20	160	72	**2**	78
5	**22**	20	110	96	**4**	50
6	**12**	20	160	72	**5**	72[d]
7	**15**	20[b]	160	72	**6**	64

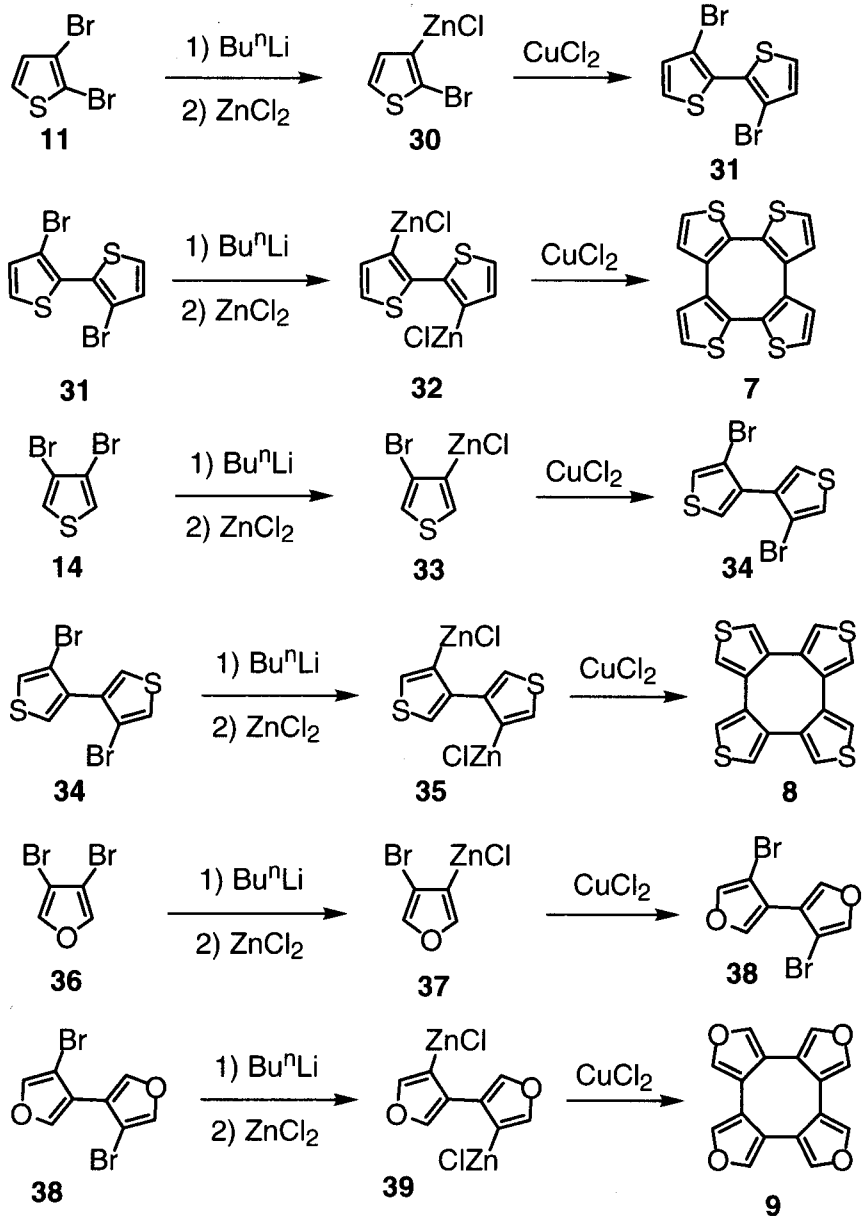
[a]Conditions: the reaction was carried out using $Me_3SnSnMe_3$ (0.9 equiv.) and $Pd(PPh_3)_4$ (15-20 mol%) in dioxane at 110-160°C in a sealed tube. [b]In the absence of PPh_3. [c]Determined by gas-chromatographic analysis. [d]Determined by gas-chromatographic analysis (69% of the isolated yield).

of **16** (entry 2). The reaction required 20 mol% of catalyst, and the treatment of **16** with hexamethylditin (0.9 equiv.) in the presence of $Pd(PPh_3)_4$ (20 mol%) and PPh_3 (0.5 equiv.) produced **1** in 75% yield (entry 3). On the basis of these results, the palladium-catalyzed cyclization of **19** was carried out with $Me_3SnSnMe_3$ (0.9 equiv.) in the presence of 20 mol% of $Pd(PPh_3)_4$ to produce **2** in 78% yield (entry 4). In the case of **22**, a similar reaction with $Me_3SnSnMe_3$ and $Pd(PPh_3)_4$ [160 °C, 24 h] gave **4** only in 20% yield, but a lower temperature and longer time [110 °C, 96 h] enhanced the cyclization to give **4** in 50% yield (entry 5). Interestingly, the cyclization of the silole derivatives (**12** and **15**) proceeded smoothly under palladium-catalyzed conditions to produce the corresponding tricyclic compounds (**5** and **6**) in good yields (entries 6 and 7). In the absence of PPh_3, the reaction of **15** produced **6** in a better yield (entry 7). The oxidative addition of the C-Br bonds in **12**, **15**, **16**, **19**, and **22** to the Pd(0) complex, followed by

transmetallation and reductive elimination, produces monostannylated compounds which lead to the cyclization products by palladium-catalyzed intramolecular cross-coupling reaction.

Synthesis of Cyclooctatetrathiophenes and Cyclooctatetrafuran.

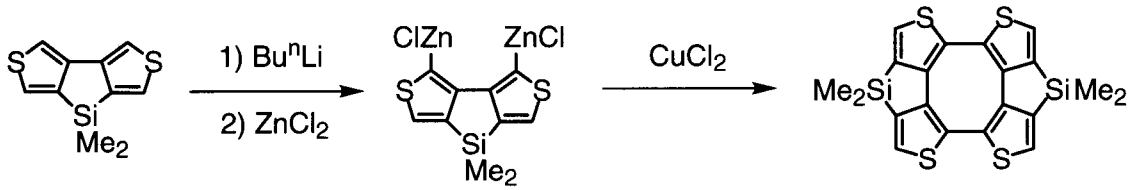
As described in this work, we developed three new methods for the intramolecular cyclization of dibromodithiophenes (methods 1, 2 and 3). In order to apply our new methods to the synthesis of polycyclic thiophenes, we carried out the synthesis of cyclooctatetrathiophenes (**7** and **8**), cyclooctatetrafuran (**9**) and the related new cyclic system (**10**). Since the palladium-catalyzed coupling reaction (method 3) could be applied only to the intramolecular cyclization of dibromides, we decided to employ the copper(II)-catalyzed coupling of organozinc species (method 2) for the construction of **7**-**10**.



Scheme 5

For the synthesis of **7**, we started from 2,3-dibromothiophene (**11**). The reaction of **11** with Bu^{n}Li (1.05 equiv.) at -78 °C in THF, followed by treatment with $ZnCl_2$ (1.1 equiv.) at -50 °C gave **30**. The zinc compound (**30**) was treated with $CuCl_2$ (1.5 equiv.) at -78 °C to room temperature to produce 3,3'-dibromo-2,2'-bithiophene (**31**) in 70% yield. The reported yield of **31** by a combination of lithiation and $CuCl_2$-coupling (61%)[22] was somewhat improved by using this method. Interestingly, the dimerization of **31** to cycloocta[1,2-*b*:4,3-*b'*:5,6-*b''*:8,7-*b'''*]tetrathiophene (**7**) can be achieved by using the coupling of the organozinc species. Thus, successive treatment of **31** with Bu^{n}Li (1.1 equiv.), $ZnCl_2$ (2.4 equiv.) and $CuCl_2$ (3 equiv.) led to **7** in 40% yield which is much higher than that based on the lithiation-$CuCl_2$ procedure (18%).[23] In a similar manner, treatment of **14** and **36** with Bu^{n}Li, followed by the reaction with $ZnCl_2$ gave **33** and **37** which were treated with $CuCl_2$ to produce **34** and **38** in 65 and 78% yields, respectively. Starting from **34** and **38**, **8** and **9** were synthesized in 43 and 14% yields, respectively, by a similar procedure to that used for **7**. 4,4'-Dibromo-3,3'-bifuran (**38**) was synthesized in good yield using our method. Although the yield of **9** is not adequate, our procedure provides a simple, accessible route to this interesting molecule.

The construction of the cyclooctatetrathiophene framework can be successfully applied to the synthesis of silicon-bridged cyclooctatetrathiophene (**10**). Direct lithiation of cyclopentadithiophene (**6**) with Bu^{n}Li in refluxing ether produced a lithio derivative which was converted into the zinc intermediate (**40**) by reacting with $ZnCl_2$ at 0 °C. This zinc species (**40**) was treated with $CuCl_2$ to give **10** in 5% yield (Scheme 6). The compound (**10**) has a planar cyclooctatetraene structure and hence a longer wavelength absorption (λ_{max} = 481 nm) with orange red-color, in contrast to colorless **7**-**9**. The ^{1}H NMR spectrum indicates an upper field shift of thiophene protons at δ 6.93, indicating the existence of a paramagnetic ring current. However, **10** has a stable compound with the melting point of 255-255.5 °C.



6 **40** **10**

Scheme 6

EXPERIMENTAL

General Procedure. ^{1}H and ^{13}C NMR spectra were recorded on JEOL LA-500 and JEOL LA-400 instruments. Spectra are reported (in δ) referenced to Me_4Si. Unless otherwise noted, $CDCl_3$ was used as solvent. Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), integration, and coupling constant (Hz). MS spectra were determined on a JEOL JMS-AX 500 instrument. Only the more intense or structurally diagnostic mass spectral fragment ion peaks are reported. Melting points were determined on a Yanaco Micro melting point apparatus MP-500D and are uncorrected. Elemental analyses were performed in the microanalysis laboratory of Tokyo Metropolitan

University. Column chromatography was carried out with use of EM Reagents silica gel 60, 70-230 mesh ASTM, Daiso silica gel 1001W, or neutral alumina activity II-III, 70-230 mesh ASTM. Gel permeation liquid chromatography (GLPC) was performed on AL LC-08 and LC-918 liquid chromatography instruments with JAIGEL-1H column (20 mm x 600 mm x 2) and chloroform as eluent. All solvents were dried by conventional procedures.

Synthesis of Bis(bromothienyl)dimethylsilane (12 and 15).

To a solution of 2,3-dibromothiophene (**11**, 10 g, 40 mmol) in dry ether (30 mL) was added *n*-butyllithium (25 mL, 40 mmol, 1.6 M in hexane) at -78 °C under nitrogen, and the mixture was stirred for 1 h at the same temperature. To the solution was added a solution of Me_2SiCl_2 (2.76 g, 20 mmol) in dry ether (10 mL) at -78 °C, and the resulting mixture was stirred at -78 °C for 1 h. The mixture was allowed to warm to rt gradually. Water was added and the organic layer was separated and the aqueous layer was extracted with ether. After drying over anhydrous $MgSO_4$, the solvent was evaporated *in vacuo* to give a residue which was chromatographed on silica gel with hexane as eluent, followed by recrystallization from hexane to give the pure bis(3-bromo-2-thienyl)dimethylsilane (**12**) in 65% yield (4.97 g). In a similar procedure, bis(4-bromo-3-thienyl)silane (**15**) was obtained in 74% yield.

Bis(3-bromo-2-thienyl)dimethylsilane (12) : colorless liquid, bp 198 °C/2.5 torr, MS *m/z* 382 (M^+), 367, 288; ^1H NMR (CD_2Cl_2) δ 7.67 (d, 2H, J = 4.4), 7.26 (d, 2H, J = 4.4), 0.50 (s, 6H); ^{13}C NMR (CD_2Cl_2) δ 152.2, 135.0, 134.6, 121.6, -2.0. Anal. Calcd for $C_{10}H_{10}Br_2S_2Si$: C, 31.41; H 2.61. Found: C, 31.66; H, 2.62.

Bis(4-bromo-3-thienyl)dimethylsilane (15): colorless crystals, mp 65-66 °C, MS *m/z* 382 (M^+), 367, 288; ^1H NMR (CD_2Cl_2) δ 7.64 (d, 2H, J = 2.9), 7.59 (d, 2H, J = 2.9), 0.63 (s, 6H); ^{13}C NMR (CD_2Cl_2) δ 139.5, 137.9, 126.2, 116.2, -1.0. Anal. Calcd. for $C_{10}H_{10}Br_2S_2Si$: C, 31.41; H 2.61. Found: C, 31.43; H, 2.59.

Intramolecular Coupling of 12 and 15.

To a solution of the dibromide (**15**, 382 mg, 1 mmol) in 60 mL of dry THF was added *n*-butyllithium (1.8 mL, 3 mmol, 1.68 M in hexane) at -78 °C and the mixture was stirred 3 h at -78 °C. Copper(II) chloride (0.81 g, 6 mmol) was added at -78 °C. After stirring 2 h at the same temperature, the reaction mixture was allowed to warm to rt and stirred overnight. After usual aqueous work-up, the crude product was purified by column chromatography on silica gel to give silacyclopentadithiophene (**6**) in 30% yield (67 mg). A similar reaction of **12** produced the enyne (**13**) in 9% yield, together with unidentified by-products.

7-Dimethylsila-*7H*-cyclopenta[1,2-*c*:3,4-*c'*]dithiophene (6): colorless crystals, mp 103-104 °C, MS *m/z* 222 (M^+), 208, 147; ^1H NMR (CD_2Cl_2) δ 7.64 (d, 2H, J = 2.4), 7.54 (d, 2H, J = 2.4), 0.41 (s, 6H); ^{13}C NMR (CD_2Cl_2) δ 148.2, 147.8, 131.8, 116.1, -1.1. Anal. Calcd for $C_{10}H_{10}S_2Si$: C, 54.05; H, 4.50. Found: C, 53.90; H, 4.50.

***Z*-1-Butylthio-4-butyldimethylsilyl-1-buten-2-yne (13)**: colorless liquid, MS *m/z* 254 (M^+); ^1H NMR ($CDCl_3$) δ 6.54 (d, 1H, J = 10.0), 5.51 (d, 1H, J = 10.0), 2.78 (t, 2H, J= 7.5), 1.65 (quint, 2H, J = 7.5), 1.43 (m, 2H), 1.28-1.39 (m, 4H), 0.93 (t, 3H, J = 7.5), 0.90 (t, 3H, J = 7.0), 0.66 (t, 2H, J =

7.56), 0.18 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 141.9, 104.6, 102.3, 101.8, 33.6, 32.5, 26.3, 26.0, 21.7, 16.0, 13.8, 13.6, -1.6; HRMS *m/z* calcd for $C_{14}H_{26}SSi$ 254.1497, found 254.1524.

Synthesis of 1, 2 and 4 using CuCN and O_2 (Table 1, Procedure A).

To a solution of dilithiated dithienyl derivative [prepared from 1 mmol of dibromodithienyl compound (**15**, **16**, **19** or **22**) with *n*-butyllithium (1.44 mL, 2.2 mmol, 1.53 M in hexane) in THF (60 mL) at -78 °C] was added CuCN (0.23 g, 2.5 mmol) at -78 °C, and the mixture was allowed to warm to rt. After the CuCN had completely dissolved, the reaction mixture was recooled to -78 °C, and the flask was degassed and filled with dry O_2. The reaction mixture was stirred for 1 h at -78 °C under O_2 atmosphere and then allowed to warm to rt by removing the dry ice-acetone bath. Water was added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted with benzene and the combined organic extracts were dried over anhydrous $MgSO_4$. After evaporating the solvent, the crude product was subjected to column chromatography on silica gel using hexane [or hexane-dichloromethane (1:1)] as eluent to afford a pure coupling product.

Dithieno[2,3-*b*:3',2'-*d*]thiophene (1): colorless crystals, mp 84-86 (lit.,[24] 85-86 °C), MS *m/z* 196 (M^+), 152, 120; ^{1}H NMR ($CDCl_3$) δ 7.40 (d, 2H, J = 5.2), 7.38 (d, 2H, J = 5.2).

Dithieno[3,4-*b*:3',4'-*d*]thiophene (2): colorless crystals, mp 87-88 (lit.,[6] 87-87.5 °C), MS *m/z* 196 (M^+), 152, 120; ^{1}H NMR ($CDCl_3$) δ 7.48 (d, 1H, J = 2.5), 7.04 (d, 1H, J = 2.5); ^{13}C NMR (CD_2Cl_2) δ 154.5, 150.8, 148.1, 137.3.

***7H*-Cyclopenta[1,2-*b*:4,3-*b'*]dithiophene (4)**: colourless crystals, mp 66-67 °C (lit.,[7] 66-67 °C), MS *m/z* 178 (M^+), 134, 93; ^{1}H NMR ($CDCl_3$) δ 7.28 (d, 2H, J = 5.1), 7.12 (d, 2H, J = 5.1), 3.77 (s, 2H).

***7H*-Cyclopenta[1,2-*b*:4,3-*b'*]dithiophen-7-one (23)**: red crystals, mp 114.5-115.5 °C (lit.,[16] 115-116 °C), MS *m/z* 192 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.56 (d, 2H, J = 4.6), 6.88 (d, 2H, J = 4.6).

Compound (25): colourless crystals, mp 188.2-190.0 °C, MS *m/z* 496 (M^+); ^{1}H NMR ($CDCl_3$) δ 8.00 (d, 2H, J = 3.0), 7.57 (d, 2H, J = 3.0), 7.23 (d, 2H, J = 3.0), 6.77 (d, 2H, J = 3.0), 0.32 (s, 12H); ^{13}C NMR ($CDCl_3$): 144.6, 143.9, 139.8, 139.3, 137.2, 136.6, 127.1, 118.0, 117.2, -2.4; IR (nujol) 3050, 2986, 2960, 2280, 1610, 1580, 1495, 1430, 1280 cm^{-1}; UV λ_{max} 243 (log ε = 4.32) nm. Anal. Calcd for $C_{22}H_{20}N_2S_4Si_2$: C, 53.18; H, 4.06; N: 5.64. Found: C, 52.98; H, 4.09; N: 5.64.

Synthesis of 1 and 2 using CuCN, O_2 and $CuCl_2$ (Table 1, Procedure B).

To a solution of **17** [prepared from **16** (356 mg, 1 mmol) with *n*-butyllithium (1.44 mL, 2.2 mmol, 1.53 M in hexane) in THF (60 mL) at -78 °C] was added CuCN (0.23 g, 2.5 mmol) at -78 °C, and the mixture was allowed to warm to rt. After the CuCN had completely dissolved, the reaction was recooled to -78 °C, and the flask was degassed and filled with dry O_2. The reaction mixture was stirred for 1 h at -78 °C under O_2 atmosphere and then $CuCl_2$ (0.81 g, 6 mmol) was added. The mixture was stirred for 1 h at -78 °C and then at rt overnight. Water (80 mL) was added to the reaction mixture and the organic layer was extracted with benzene. After washing the organic layer successively with 4 M hydrochloric acid and water, the organic layer was dried over anhydrous $MgSO_4$. The crude product was subjected to column

chromatography on silica gel (25 g) using hexane as eluent to afford the pure **1** in 47% yield (92 mg). In a similar manner, succesive treatments of **20** prepared from **19** with CuCN, O_2 and $CuCl_2$ produced **2** in 49% yield.

Synthesis of 1, 2, 4 and 6 by the Coupling of Organozinc Species with $CuCl_2$ (Table 2). To a solution of **17** [prepared from **16** (1 mmol) with *n*-butyllithium (1.44 mL, 2.2 mmol, 1.53 M in hexane) in THF (50 mL) at -78 °C] was added a solution of anhydrous $ZnCl_2$ (0.327 g, 2.4 mmol) in THF (10 mL) at -50 °C, and the mixture was stirred for 2 h at the same temperature. The reaction mixture was recooled to -78 °C and copper(II) chloride (0.4034 g, 3 mmol) was added. After stirring 2 h at -78 °C, the reaction mixture was allowed to warm to room temperature by removing the dry ice-acetone bath and stirred overnight (14 h). The reaction mixture was hydrolyzed with 4 M hydrochloric acid and extracted with benzene. After drying with anhydrous $MgSO_4$, the solvent was evaporated *in vacuo* to leave a crude product which was chromatographed on silica gel using hexane as eluent, followed by recrystallization from hexane to give the pure **1** in 69% yield (135 mg). In a similar procedure, **2**, **4** and **6** were synthesized in 70, 55 and 61% yields, respectively.

Synthesis of 1, 2, 4, 5 and 6 using $Pd(PPh_3)_4$ and Hexamethylditin (Table 3). A solution of **16** (89 mg, 0.25 mmol), hexamethylditin (73.6 mg, 0.225 mmol), $Pd(PPh_3)_4$ (57.6 mg, 0.05 mmol) and PPh_3 (32.8 mg, 0.125 mmol) in dioxane (2.5 mL) was placed in a sealed tube and heated at 160 °C for 24 h. After cooling to rt, the product was extracted with benzene and the extracts were chromatographed on silica gel using hexane as eluent to yield the pure **1** in 75% yield (147 mg). In the absence of PPh_3, a similar reaction produced **1** in 67% yield.

In a similar procedure, **19** and **12** produced **2** and **5** in 78 and 72% yields, respectively. In the case of **22**, the reaction was carried out at 110 °C for 96 h to afford **4** in 50% yield. The reaction of **15** was carried out without PPh_3 at 160 °C for 24 h to give **6** in 64% yield. In the presence of PPh_3 (0.5 equiv.), a similar reaction gave **6** in 48% yield.

7-Dimethylsila-*7H*-cyclopenta[1,2-*b*:4,3-*b'*]dithiophene (5): colourless oil, bp 84-86 °C/2.5 torr, MS *m/z* 222 (M^+), 208, 147; ^1H NMR (CD_2Cl_2) δ 7.50 (d, 2H, J = 4.9), 7.12 (d, 2H, J = 4.9), 0.80 (s, 6H); ^{13}C NMR (CD_2Cl_2) δ 132.7, 132.0, 131.2, 118.5, -1.0. Anal. Calcd for $C_{10}H_{10}S_2Si$: C, 54.05; H, 4.50. Found: C, 54.09; H, 4.55.

Synthesis of 3,3'-Dibromo-2,2'-bithiophene (31), 4,4'-Dibromo-3,3'-bithiophene (34) and 4,4'-Dibromo-3,3'-bifuran (38). To a solution of 2,3-dibromothiophene (4.839 g, 20 mmol) in dry THF (150 mL) was added *n*-butyllithium (13.2 mL, 21 mmol, 1.59 M in hexane) at -78 °C and the mixture was stirred for 3 h at the same temperature. A solution of $ZnCl_2$ (2.998 g, 22 mmol) in dry THF (25 mL) was added to the reaction mixture at -50 °C and the resulting mixture was stirred for 2 h at the same temperature. The reaction mixture was recooled to -78 °C and copper(II) chloride (4.034 g, 30 mmol) was added. After stirring for 2 h at -78 °C, the reaction mixture was allowed to warm to rt and stirred overnight. After usual aqueous work-up, the crude product was purified by column chromatography on silica gel, followed by

recrystallization from hexane to produce 3,3'-dibromo-2,2'-bithiophene (**31**) in 70% yield (2.27 g). In a similar procedure described above, 3,4-dibromothiophene (**14**) and 3,4-dibromofuran (**36**)[25] produced 4,4'-dibromo-3,3'-bitiophene (**34**) and 4,4'-dibromo-3,3'-difuran (**38**) in 65 and 78% yields, respectively.

3,3'-Dibromo-2,2'-bithiophene (31): colorless crystals, mp 103-104 °C (lit.,[22] 102-104 °C), MS *m/z* 326, 324, 322 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.41 (d, 2H, J = 5.5), 7.08 (d, 2H, J = 5.5); ^{13}C NMR ($CDCl_3$) δ 130.8, 128.9, 127.5, 112.7.

4,4'-Dibromo-3,3'-bithiophene (34): colorless crystals, mp 127.5-129 °C (lit.,[22] 127-129 °C), MS *m/z* 326, 324, 322 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.38 (d, 2H, J = 3.5), 7.36 (d, 2H, J = 3.5); ^{13}C NMR ($CDCl_3$) δ 135.3, 125.6, 123.3, 112.3.

4,4'-dibromo-3,3'-difuran (38): colorless crystals, mp 77.5-78.5 °C, MS *m/z* 294, 292, 290 (M^+), 213, 212; ^{1}H NMR ($CDCl_3$) δ 7.87 (d, 2H, J = 1.7), 7.52 (d, 2H, J = 1.7); ^{13}C NMR ($CDCl_3$): 141.7, 140.9, 116.0, 100.7; IR (neat) 3143, 1636, 1594, 1538, 1511, 1492 cm^{-1}; HRMS *m/z* calcd for $C_8H_4O_2{}^{79}Br^{81}Br$ 291.8558, found 291.8511.

Synthesis of 7, 8 and 9 by the Coupling of Organozinc Species with $CuCl_2$.

To a solution of **31** (324 mg, 1 mmol) in THF (20 mL) was added *n*-butyllithium (1.28 mL, 2 mmol, 1.57 M in hexane) at -78 °C, and the mixture was stirred for 2 h at -78 °C. To the solution was added a solution of anhydrous $ZnCl_2$ (0.300 g, 2.2 mmol) in THF at -50 °C, and the mixture was stirred for 2 h at the same temperature. The reaction mixture was recooled to -78 °C and copper(II) chloride (0.403 g, 3 mmol) was added. After stirring for 2 h at -78 °C, the reaction mixture was allowed to warm to rt by removing the dry ice-acetone bath and stirred overnight (12 h). The reaction mixture was hydrolyzed with 4 M hydrochloric acid and extracted with benzene. After drying with anhydrous $MgSO_4$, the solvent was evaporated *in vacuo* to leave a crude product which was chromatographed on silica gel using hexane as eluent, followed by recrystallization from hexane to give the pure **7** in 40% yield (131 mg). In a similar procedure, **8** and **9** were synthesized in 43 and 14% yields, respectively.

Cycloocta[1,2-*b*:4,3-*b'*:5,6-*b''*:8,7-*b'''*]tetrathiophene (7): colorless crystals, mp 256-257 °C (lit.,[23] 255-256 °C), MS *m/z* 328 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.37 (d, 4H, J = 5.2), 6.96 (d, 4H, J = 5.2); ^{13}C NMR ($CDCl_3$) δ 136.6, 132.4, 129.9, 127.1.

Cycloocta[1,2-*c*:3,4-*c'*:5,6-*c''*:7,8-*c'''*]tetrathiophene (8): colorless crystals, mp 298.5-300 °C (lit.,[23] 300-301 °C), MS *m/z* 328 (M^+); ^{1}H NMR ($CDCl_3$) δ 7.22 (s, 8H); ^{13}C NMR ($CDCl_3$) δ 137.2, 124.4.

Cycloocta[1,2-*c*:3,4-*c'*:5,6-*c''*:7,8-*c'''*]tetrafuran (9): pale yellow crystals, mp 188-189 °C, MS *m/z* 264 (M^+); ^{1}H NMR ($CDCl_3$): 7.48 (s, 8H); ^{13}C NMR ($CDCl_3$): 140.4, 117.2; HRMS *m/z* calcd for $C_{16}H_8O_4$ 264.0434, found 264.0423.

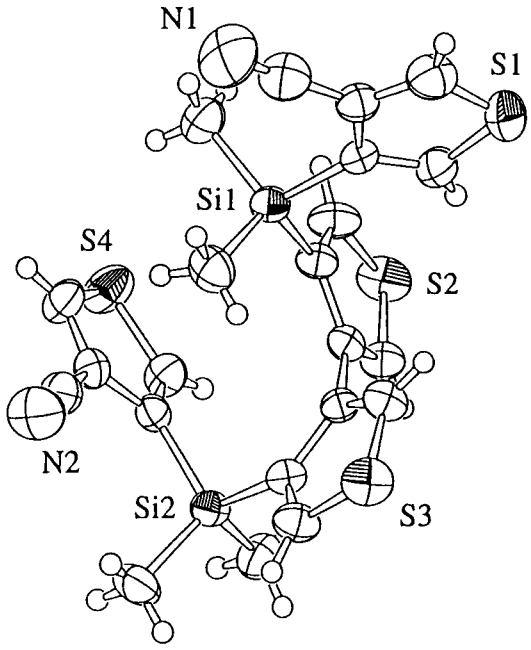
Synthesis of the silicon-bridge compound (10).

To a solution of silacyclopentadithiophene (**6**, 222 mg, 1 mmol) in dry ether (25 mL) was added *n*-butyllithium (1.3 mL, 2 mmol, 1.54 M in hexane) at rt. The mixture was refluxed for 1.5 h and allowed to

cool to rt. A solution of $ZnCl_2$ (0.230 g, 2.2 mmol) in dry THF (10 mL) was added to the reaction mixture at 0 °C and the resulting mixture was stirred for 2 h at the same temperature. Copper(II) chloride (0.403 g, 3 mmol) was added at 0 °C. After stirring for 2 h at the same temperature, the reaction mixture was allowed to warm to rt and stirred overnight. After usual aqueous work-up, the crude product was subjected to column chromatography on silica gel using hexane-benzene (3:1) as eluent, followed by GLPC separation to give the pure **10** in 5% yield (11 mg), orange-red crystals, mp 255-255.5 °C ; MS *m/z* 440 (M^+); ^1H NMR ($CDCl_3$) δ 6.93 (s, 4H), 0.31 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 151.4, 141.9, 131.0, 129.1, -2.0; UV λ_{max} (ethanol) 481 (log ε = 2.50), 308.5 (4.32), 224 (4.44) nm; HRMS *m/z* calcd for $C_{20}H_{16}S_4Si_2$ 439.9632, found 439.9674.

X-Ray Structural Determination of 25.

Crystals of **25** suitable for X-Ray structure analysis were obtained by slow recrystallization of **25** from (hexane-benzene 1:1); colorless prism of crystal size 0.40 x 0.50 x 0.80 mm; intensity data were collected using a Rigaku7R four-circle diffractometer with graphite-monochromated Mo-Ka radiation (l = 0.71069; crystal system monoclinic, space group $P2_{1/n}$ (No. 14); cell parameters: a = 7.923(3), b = 20.780(4), c = 15.264(3), β = 104.26(2)°; V = 2435(1); Z = 4; Dcalcd = 1.355 g cm^{-3}; F000 = 1032.00; μ(Mo-Kα) = 5.01 cm^{-1}; no. of unique reflections 5591 (R_{int} = 0.076); no. of reflections measured with I > 3.00σ(I) 3933; R = 0.042, Rw = 0.042. Structural parameters of non-hydrogen atoms were refined anisotropically according to the full-matrix least-squares technique.



ORTEP Drawing of **25**

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