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Synthesis and Characterization of Dimers, Trimers, and Tetramers of 3,6-Dimethylthieno[3,2-*b*]thiophene and 3,6-Dimethylselenolo[3,2-*b*]selenophene

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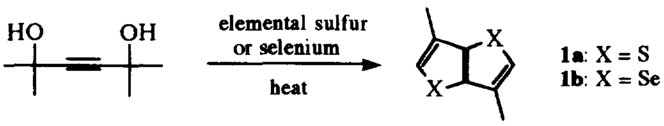
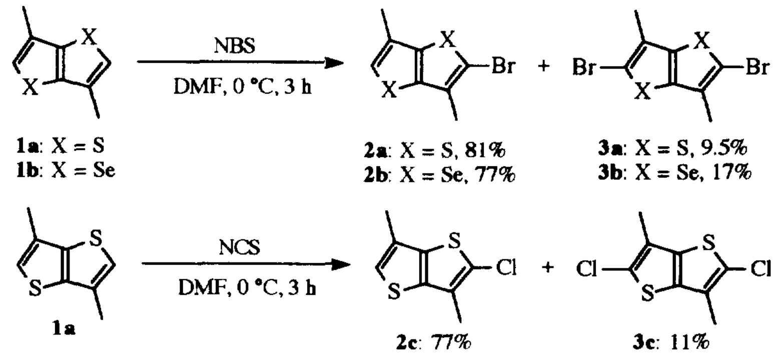
Abstract: 3,6-Dimethylthieno[3,2-*b*]thiophene (**1a**) and 3,6-dimethylselenolo[3,2-*b*]selenophene (**1b**) have recently become readily obtainable. Starting from these compounds, their dimers, trimers, and tetramers, in which each thienothiophene unit and selenoloselenophene unit were regularly connected at their α-position, were satisfactorily synthesized and characterized by UV/Vis spectral and CV oxidation potentials data. X-Ray single crystal structure analysis of the dimer of **1b** revealed that two selenoloselenophene units are twisted with a large dihedral angle of 69.5° with an *s*-cis structure.

Thiophene oligomers are compounds of current interest because many of them show photoenhanced biological activities[1] and α-type of thiophene oligomers such as 2,2':5',2"-terthiophene produce crystalline, electroconductive doped polythiophenes on electrochemical polymerizations.[2] Thus, a wide variety of thiophene oligomers and related compounds including mixed thiophene-pyrrole oligomers have been synthesized mainly with expectation of obtaining excellent precursor compounds for molecular devices and electroconductive polymers. However, no report has appeared on the preparation of oligomers of thieno[3,2-*b*]thiophene in which two thiophene rings are fused at their 2- and 3-positions; several reports have been concerned with preparation of polythieno[3,2-*b*]thiophenes from its monomer by chemical and electrochemical polymerization and their properties.[3] We have recently reported a one-pot synthesis of 3,6-dimethylthieno[3,2-*b*]thiophene (**1a**) by reaction of commercially available 2,5-dimethyl-3-hexyne-2,5-diol with elemental sulfur, which enabled us to prepare **1a** in large quantities.[4] We therefore planned the preparation of oligomers of **1a**, in which each unit of **1a** is regularly connected at its α-position. We have expected that two methyl groups of **1a** increase the solubility of the oligomers in common organic solvents; solubility problem of the oligomers often makes the preparation of higher oligomers very difficult and also restricts their use as the molecular devices, although introduction of bulky substituents might result in a neck of inhibiting the planarity of the whole system. 3,6-Dimethylselenolo[3,2-*b*]selenophene (**1b**) has been also prepared in one-pot by reaction of 2,5-dimethyl-3-hexyne-2,5-diol with elemental selenium.[4] We have thus also planned the preparation of the oligomers of **1b**.[5] We report here the synthesis and characterization of dimers, trimers, and tetramers of **1a** and **1b**.

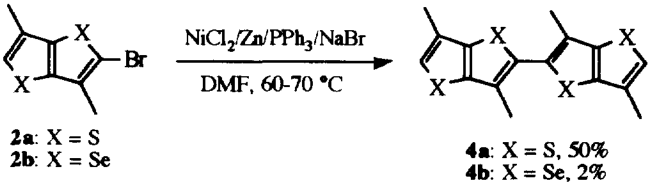


Synthesis of Oligomers

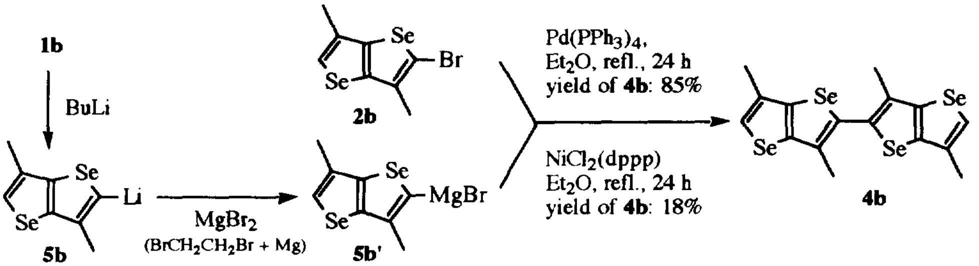
Preparation of Dimers. Symmetrically substituted biaryls are conveniently prepared by reductive coupling of aryl halides.[6] Thus, in order to obtain the monobromothienothiophene (**2a**) as the starting material leading to the dimer, bromination of **1a** was carried out with 1 equimolar amount of *N*-bromosuccinimide (NBS) in a mixture of acetic acid and dichloromethane. This furnished the expected monobromide **2a** in 67% yield along with the dibrominated thiophene (**3a**) in 11% yield with 11% recovery of **1a**. A better yield and more selective synthesis of **2a** was attained by carrying out the bromination in *N,N*-dimethylformamide (DMF),[7] which gave **2a** in 81% yield along with **3a** in 9.5% yield. Under the same conditions, the bromination of the selenoloselenophene **1b** gave the monobrominated selenophene (**2b**) in 77% yield along with the dibrominated compound (**3b**) in 17% yield, and the chlorination of **1a** with *N*-chlorosuccinimide (NCS) gave the monochlorinated thiophene (**2c**) in 77% yield along with the dichlorinated compound (**3c**) in 11% yield.



The reductive coupling of **2a** was carried out by using an activated nickel(0) catalyst, which was prepared from anhydrous nickel(II) chloride, zinc powder, and triphenylphosphine in the presence of sodium bromide in DMF.[8] Heating **2a** with this reagent in DMF satisfactorily furnished the expected dimer (**4a**) as pale-yellow crystals in 50% yield. However, application of the reaction to the selenoloselenophene dimer synthesis is unsuccessful; the expected dimer (**4b**) was obtained only in 2% yield.



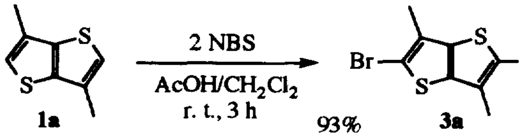
We therefore planned the preparation of **4b** by metallic reagent-catalyzed coupling of the Grignard reagent (**5b'**) with **2b**. However, in spite of much effort, **5b'** could not be obtained because of the inactivity of **2b** toward magnesium. Therefore, **5b'** had to be synthesized in an indirect way. Fortunately, the selenoloselenophene **1b** was readily lithiated by butyllithium; ^{1}H NMR analysis of the mixture, obtained by action of 1 equimolar amount of butyllithium on **1b** followed by quenching with D_2O, revealed that **1b** was lithiated to give the lithio derivative **5b** at least in 95% yield. Thus, **5b'** was obtained by adding $MgBr_2$ (prepared from 1,2-dibromoethane and magnesium in ether) to the ether solution of **5b**. Heating **5b'** with **2b** in the presence of $Pd(PPh_3)_4$ catalyst[9] in ether resulted in the formation of the expected dimer **4b** in 85% yield as pale-yellow crystals. Although we have also employed [1,3-bis(diphenylphosphino)propane]nickel(II) chloride [$NiCl_2$(dppp)] as the coupling catalyst,[10] in this case, the yield of **4b** was as low as 18%. The $NiCl_2$(dppp)-catalyzed coupling of **5b** with **2b** also gave **4b** in a moderate yield (21%).

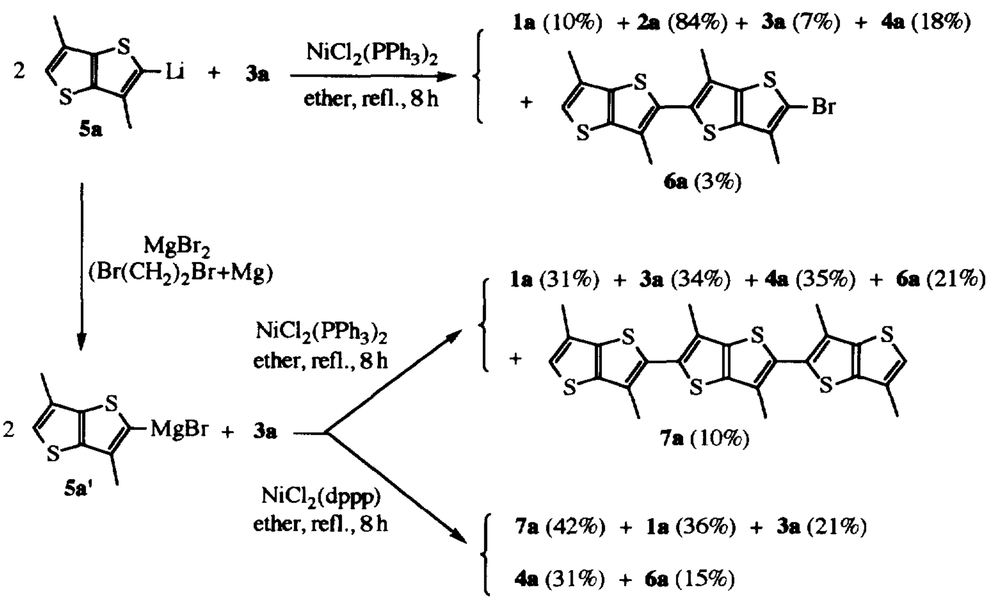


$$\mathbf{5b} + \mathbf{2b} \xrightarrow[\text{NiCl}_2\text{(dppp)}\ \text{Et}_2\text{O, refl., 24 h}]{} \mathbf{4b}\ (21\%)$$

^{1}H NMR spectra of **4a** and **4b** showed one signal due to aromatic hydrogen and two signals due to methyls and ^{13}C NMR spectra showed six signals of aromatic carbons and two signals of methyl carbons.

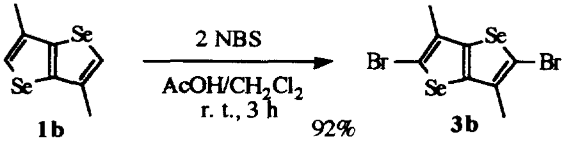
Preparation of Trimers. We first tried the preparation of the thienothiophene trimer (**7a**) by bis-coupling of the dibromothienothiophene **3a** with the thienyllithium **5a**. The both starting materials could be readily obtained; **3a** was obtained in 93% yield by bromination of **1a** with 2 equimolar amounts of NBS and **5a** more than in 95% yield by lithiation of **1a**. However, heating **3a** and **5a** in refluxing ether in the presence of $NiCl_2(PPh_3)_2$ gave a complex mixture; detailed product analysis revealed that no expected trimer was formed, but the dimer **4a** (18%) and its bromo derivative (**6a**) (3%) were formed along with **1a** (10%), **2a** (84%), and **3a** (7%). These results, particularly the formation of **2a** in a large amount, indicate that the metal-halogen exchange took place between **3a** and **5a** to a considerable extent. We then next examined the preparation of the trimer by coupling of **3a** with the Grignard reagent **5a'**, prepared by addition of $MgBr_2$ to **5a**; also in this case, **5a'** could not be prepared from **2a**. Thus, **3a** and **5a'** were heated in the presence of $NiCl_2(PPh_3)_2$ in refluxing ether for 8 h, which produced the trimer **7a** though in 10% yield in addition to **1a** (31%), **3a** (34%), **4a** (35%), and **6a** (21%). Ultimately it was found that $NiCl_2$(dppp) serves as a better coupling catalyst; the coupling catalyzed by this reagent furnished **7a** as yellow crystals in 42% yield.

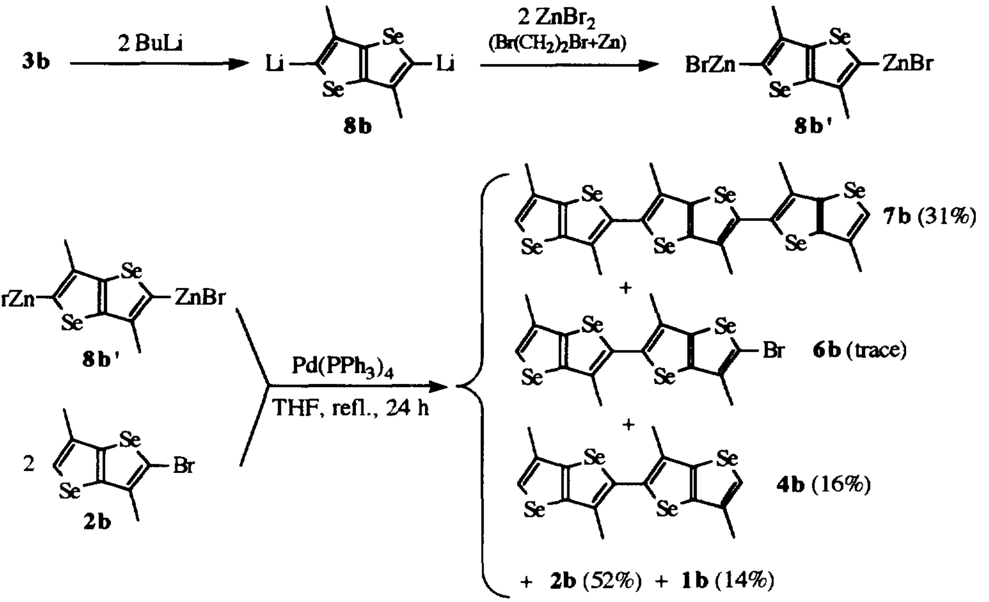




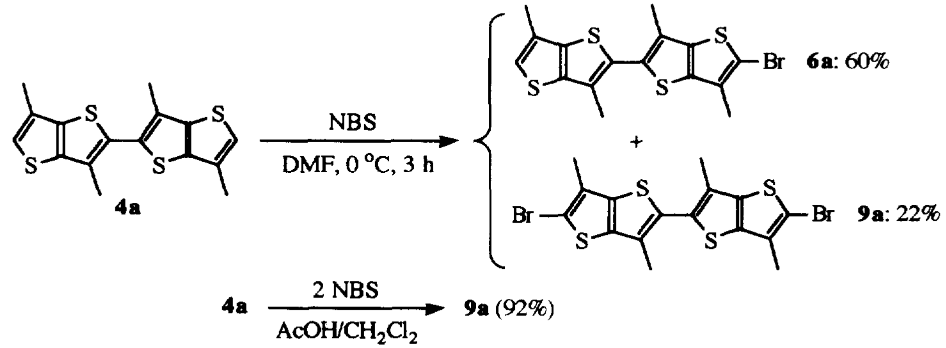
The trimer (**7b**) of the selenoloselenophene **1b** could be synthesized by $Pd(PPh_3)_4$-catalyzed coupling of the zinc bromide reagent (**8b'**) with the bromoselenophene **2b**.[11] The reaction in refluxing ether furnished **7b** in 31% yield as yellow crystals in addition to the dimer **4b** (16%), the monobromide (**6b**) of the dimer (trace), **2b** (52%), and **1b** (14%). The zinc reagent **8b'** was prepared by adding the zinc bromide, prepared from 1,2-dibromoethane and zinc powder in ether, to an ether solution of the dilithiated selenophene **8b**, which in turn prepared by action of butyllithium on the dibromoselenophene **3b**. Bromination of **1b** gave **3b** in 92% yield. Attempted preparation of **7b** by $NiCl_2$(dppp)-catalyzed coupling of the dibromide **3b** with two molecules of the Grignard reagent **5b'** did not give any amount of the trimer **7b** and also the $NiCl_2$(dppp)-catalyzed coupling of the dilithiated selenophene **8b** with two molecules of the monobromide **2b** gave **7b** in very low yield (1.4%).

Structures of **7a** and **7b** are apparent from the NMR data; in ^1H NMR the both **7a** and **7b** show the three methyl signals and in ^{13}C NMR the eight signals due to the ring carbons together with three signals due to the methyl carbons.



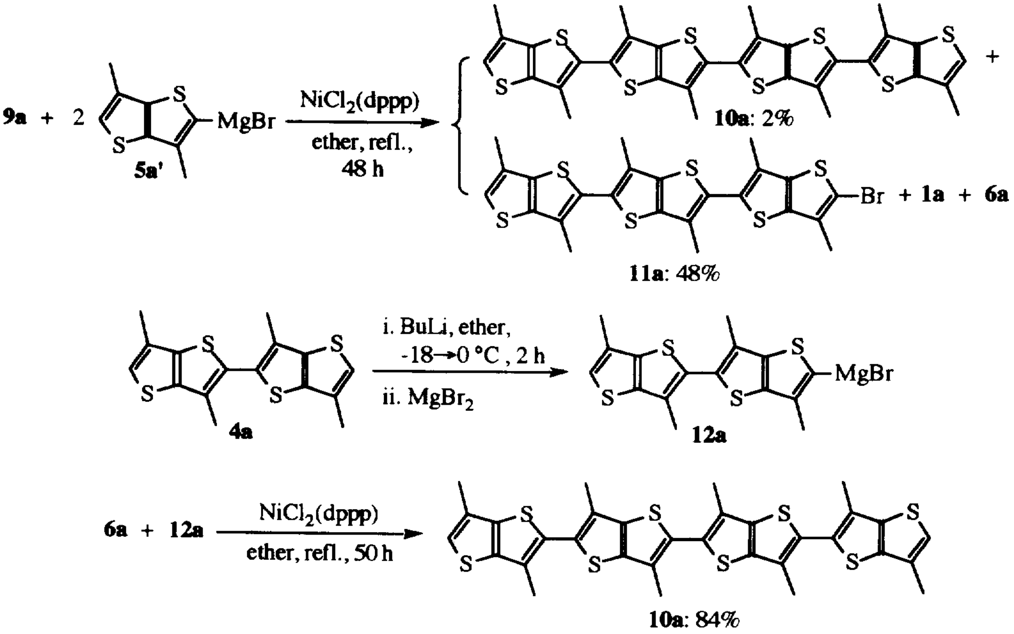


Preparation of Tetramers. Bromination of the dimer **4a** with 1 equimolar amount of NBS in DMF afforded the monobromide **6a** in 60% yield and the dibromide **9a** in 22% yield, while bromination with 2 equimolar amounts of NBS in AcOH/CH_2Cl_2 produced the dibromide **9a** in 92% yield.

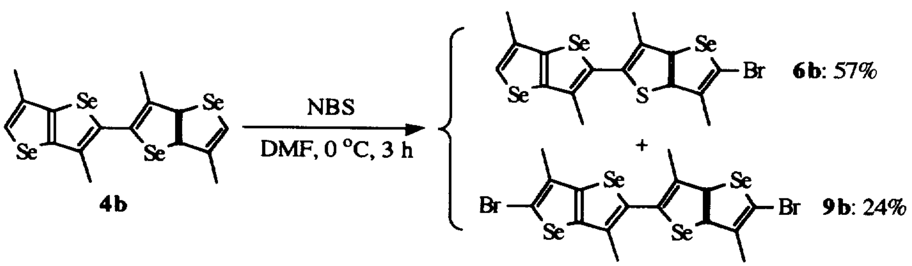


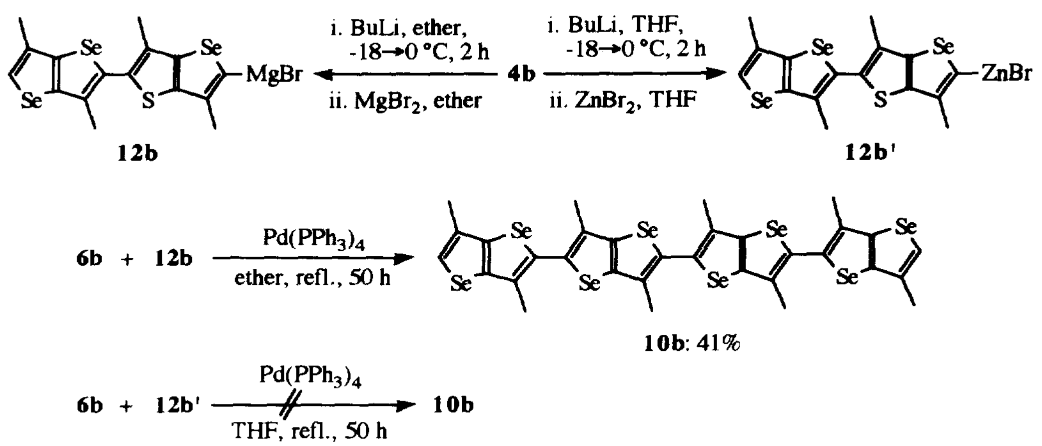
We first attempted the preparation of the tetramer **10a** of the thienothiophene **1a** by coupling of the dibromide **9a** with two molecules of the Grignard reagent **5a**'. However, the $NiCl_2$(dppp)-catalyzed coupling in ether gave the desired tetramer **10a** in only 2% yield, the major product being a compound to be considered **11a** which might be formed by coupling of **9a** with one molecule of **5a**'. This means that further coupling of **11a** with **5a**' does not proceed probably because **11a** is hardly soluble in ether.

We then next planned the preparation of **10a** by coupling of the monobromide **6a** with the Grignard reagent **12a**. Treatment of the dimer **4a** with 1 equimolar amount of butyllithium, quenching with D_2O, and ^1H NMR analysis of the mixture showed that the lithiation of **4a** takes place in more than 90% yield. Thus, **12a** could be obtained by adding an ether solution of $MgBr_2$ (prepared from 1,2-dibromoethane and magnesium in ether) to an ether solution of the lithiated **4a**. Heating **6a** and **12a** in refluxing ether for 50 h in the presence of $NiCl_2(dppp)$ satisfactorily furnished the tetramer **10a** as ocher crystals in 84% yield.



The synthesis of the tetramer **10b** of the selenoloselenophene **1b** could be attained by coupling of the monobromide **6b** with the Grignard reagent **12b**. Thus, the dimer **4b** was brominated with 1 equimolar amount of NBS in DMF to give the monobromide **6b** in 57% yield and the dibromide **9b** in 24% yield. The Grignard reagent **12b** was prepared by lithiating **4b** with 1 equimolar amount of butyllithium and then by adding $MgBr_2$ to the lithiated **4b** (quenching experiment with D_2O showed that the lithiation of **4b** proceeded in more than 90% yield). The monobromide **6b** and the Grignard reagent **12b**, thus obtained, were combined and heated in refluxing ether in the presence of $Pd(PPh_3)_4$ for 50 h, which gave the tetramer **10b** as mud yellow crystals in 41% yield. Curiously enough, attempted $Pd(PPh_3)_4$-catalyzed coupling of **6b** and the zinc reagent **12b'** (prepared by addition of $ZnBr_2$ to the lithiated **4b**) in refluxing THF did not give the tetramer **10b** in any amount.





^{1}H NMR spectrum of **10a** shows three methyl signals at δ 2.33, 2.35, and 2.38 in the 2:1:1 intensity ratio because of overlapping of two methyl signals in addition to one aromatic hydrogen signal at δ 7.00, while that of **10b** shows four methyl signals at δ 2.28, 2.29, 2.35, and 2.37 and one aromatic hydrogen signal at δ 7.51 in agreement with the assigned structure. Very poor solubility of the both compounds in organic solvents made it impossible determine ^{13}C NMR spectra.

X-Ray Crystal Structure Determination

We have planned the X-ray crystal structure determination of both of the thienothiophene dimer **4a** and selenoloselenophene dimer **4b**. Unfortunately, however, in spite of much effort, no good single crystals of **4a**, suitable for the analysis, was obtained, whilst **4b** gave nice crystals on slow evaporation of a chloroform solution.

The ORTEP drawing of **4b** is given in Fig. 1 and the relevant bond lengths, bond angles, and torsion angles data are summarized in Table 1. The most characteristic structural feature of this molecule is that it adopts an *s*-cis conformation, in which the planes of nearly-planar selenoloselenophene units are twisted each other with a large dihedral angle of 69.5° (Fig. 2). This is in marked contrast to the observation that 2,2'-bithiophene and 2,2':5',2"-terthiophene exist in nearly-planar *s*-trans form with C_{2h} and C_{2v} symmetries, respectively, in the crystalline state.[12] The large dihedral angle observed should be ascribed to the steric repulsion between two β-methyl groups. However, the bond length of C(6)-C(7), 1.46 Å, which is shorter than common carbon-carbon single bond lengths, may suggest that some conjugation between two selenoloselenophene units still exists. The intramolecular bond distances and bond angles in each selenoloselenophene retain a considerable similarity to those of the parent selenolo[3,2-*b*]selenophene.[13]

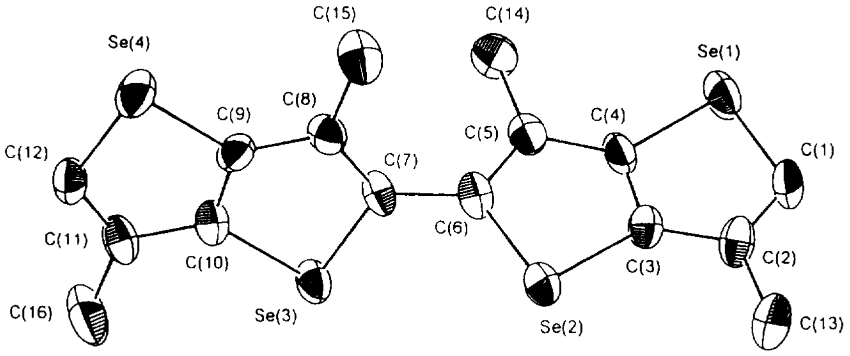


Fig. 1. ORTEP drawing of the selenoloselenophene dimer **4b**.

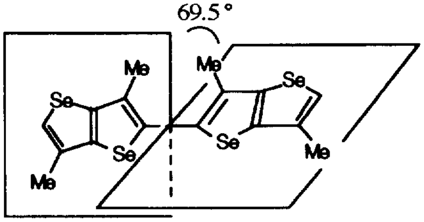


Fig. 2. Twisted *s*-cis structure of **4b**.

Table 1. Selected bond lengths (Å), bond angles (°), and torsion angles (°) of the dimer **4b**.

Bond lengths		Bond angles		Torsion angles	
Se(1)-C(1)	1.906(18)	C(1)-Se(1)-C(4)	86.9(7)	Se(2)-C(6)-C(7)-Se(3)	-69.9(11)
Se(1)-C(4)	1.879(13)	Se(1)-C(1)-(2)	112.3(11)	C(5)-C(6)-C(7)-C(8)	-65.7(18)
C(1)-C(2)	1.34(3)	C(1)-C(2)-C(3)	113.8(15)	Se(1)-C(1)-C(2)-C(3)	2.4(11)
C(2)-C(3)	1.412(19)	C(2)-C(3)-C(4)	117.9(12)	C(1)-C(2)-C(3)-C(4)	-3.4(14)
C(3)-C(4)	1.39(3)	C(3)-C(4)-Se(1)	108.9(9)	C(2)-C(3)-C(4)-Se(1)	2.6(11)
Se(2)-C(3)	1.885(13)	C(3)-C(4)-C(5)	119.6(12)	C(1)-Se(1)-C(4)-C(5)	179.4(15)
Se(2)-C(6)	1.894(15)	C(4)-C(5)-C(6)	111.1(13)	Se(1)-C(4)-C(5)-C(6)	179.9(20)
C(4)-C(5)	1.422(18)	C(5)-C(6)-Se(2)	113.4(10)	Se(1)-C(4)-C(3)-Se(2)	179.6(12)
C(5)-C(6)	1.380(19)	C(3)-Se(2)-C(6)	87.1(6)	C(4)-C(3)-Se(2)-C(6)	0.6(11)
C(6)-C(7)	1.462(17)			C(3)-Se(2)-C(6)-C(5)	-0.5(11)
C(2)-C(13)	1.53(3)			Se(2)-C(6)-C(5)-C(4)	0.3(10)
C(5)-C(14)	1.50(3)			Se(2)-C(6)-C(7)-C(8)	111.7(18)
				Se(3)-C(7)-C(6)-C(5)	112.7(17)

UV/Vis Spectra of Oligomers

UV/Vis spectra of 3,6-dimethylthieno[3,2-*b*]thiophene (**1a**) and its dimer **4a**, trimer **7a**, and tetramer **10a** and those of 3,6-dimethylselenolo[3,2-*b*]selenophene (**1b**) and its dimer **4b**, trimer **7b**, and tetramer **10b** are shown in Figs. 3 and 4, respectively; reliable molar extinction coefficients of **10b** could not be obtained because of the very poor solubility of the compound in common organic solvents. The longest λ_{max} of the selenoloselenophenes appears in a longer wavelength region than that of the corresponding thienothiophenes in accordance with the fact that the longest λ_{max} (249 nm) of the parent selenophene appears at a longer wavelength than that (231 nm) of the parent thiophene.[14] The molar extinction coefficients generally increase with increasing number of thienothiophene and selenoloselenophene units. In the both series, the bathochromic shift of the longest λ_{max} is observed with increasing number of the ring units, but it is much smaller than expected. Although this may be partly due to the inherent nature of these systems, it should be mainly ascribed to the steric repulsion between β-methyl groups which prevents the planarity of the ring units as evidenced by the X-ray analysis; the longest λ_{max} of 2,2'-bithiophene, which exists in a planar *s*-trans structure, appears at 302 nm, while that of 2,2'-bi[3-methylthiophene], which resists taking a planar conformation because of steric hindrance, occurs at 270 nm.[15]

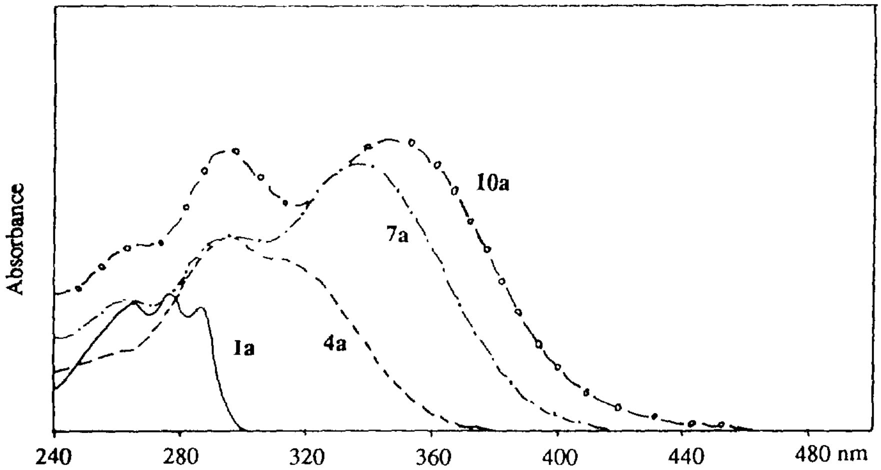


Fig. 3. UV/Vis spectra of 3,6-dimethylthieno[3,2-*b*]thiophene (**1a**) and its dimer **4a**, trimer **7a**, and tetramer **10a** (CH_2Cl_2 as the solvent).

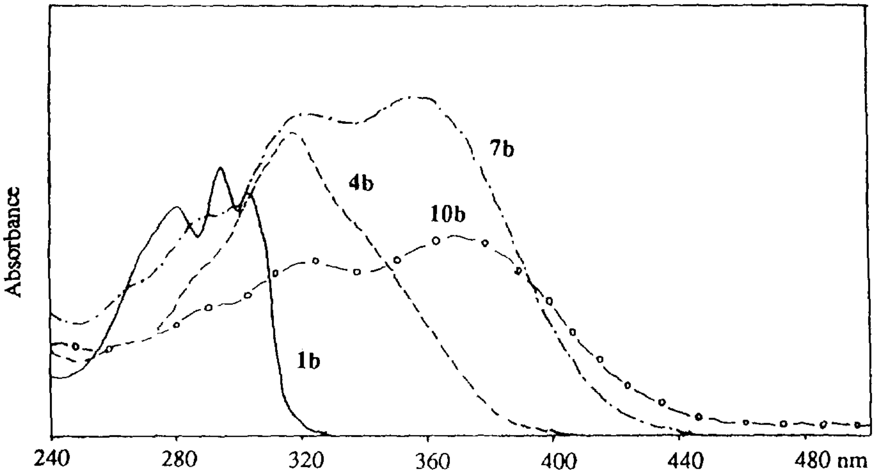


Fig. 4. UV/Vis spectra of 3,6-dimethylselenolo[3,2-*b*]selenophene (**1b**) and its dimer **4b**, trimer **7b**, and tetramer **10b** (CH_2Cl_2 as the solvent); very poor solubility of **10b** makes its absorption coefficents inaccurate.

CV Oxidation Potentials of Oligomers

CV oxidation potentials data, obtained with a platinum working electrode and 0.1 M electrolyte (tetrabutylammonium chloride) in CH_3CN or CH_2Cl_2 and corrected by the redox potentials for the ferrocene/ferrocenium couple, are summarized in Table 2. The data on **10a** are not very reliable because of the solubility problem, while those of **7b** and **10b** could not be obtained because of the poor solubility of the samples. Every compound shows irreversible oxidation peaks because radical cations formed are very reactive and undergo polymerization as many thiophenes and related compounds do electro-polymerization.[16] In fact, when an acetonitrile solution of the dimer **4b** was scanned 50 times, the formation of a dark brown film of polymeric materials was observed on the Pt working electrode with increase of the electric current (Fig. 5). As expected, E^{ox} decreases with an increasing number of thienothiophene and selenoloselenophene units because of the extended conjugation, though it is less effective than in the case of α-type thiophene oligomers due to the non-planarity of the whole system. The low oxidation potentials observed with such as **7a** and **10a** and also the formation of the polymeric materials on oxidation suggest the possibility that these compounds might serve as precursor compounds for molecular devices and conductive polymers.

Table 2. Oxidation potentials data of **1a,b, 4a,b, 7a**, and **10a**.

Compound	E^{ox} (V^a)	Compound	E^{ox} (V^a)
1a	1.04^b	**1b**	0.93^b
4a	0.65^b	**4b**	0.64^b
7a	0.53^c		
10a	0.44^c		

[a] V *vs.* ferrocene/ferrocenium couple.
[b] $E_{1/2}$ (Ferrocene/Ferrocenium); 0.2 V *vs.* Ag/Ag^+ in CH_3CN.
[c] $E_{1/2}$ (Ferrocene/Ferrocenium): 0.2 V *vs.* Ag/Ag^+ in CH_2Cl_2.

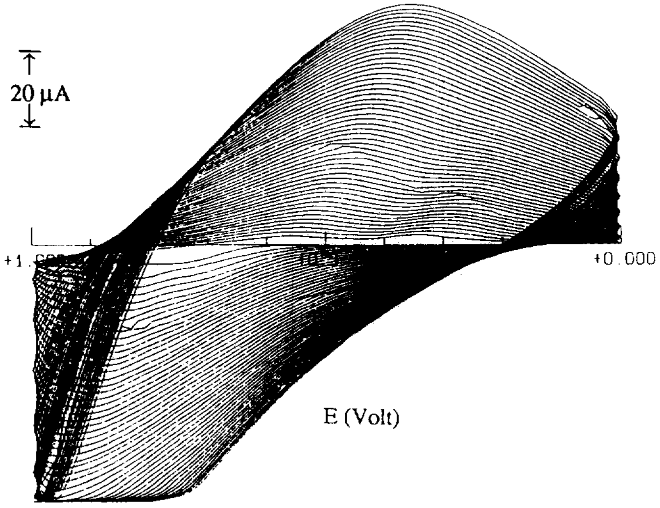


Fig. 5. Cyclic voltammogram of the selenoloselenophene dimer **4b** (scanned 50 times).

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were determined on a Bruker AC-200 (200 MHz for ^1H and 50 MHz for ^{13}C) or on a Bruker AM-400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C) in $CDCl_3$ using tetramethylsilane as an internal standard. UV/Vis spectra were obtained on a JASCO V-560 spectrophotometer. Mass spectra were determined on a Shimadzu QP-1000 mass spectrometer or on a JEOL DX-303 mass spectrometer. Transfer of organometallic reagents was all carried out by applying argon gas pressure through a Teflon tubing and rubber septa throughout this work. Column chromatography was carried out using silica gel 60 (E. Merck, particle size 0.040-0.063 mm, 230-400 mesh ASTM). Elemental analyses were performed by the Chemical Analysis Center of Saitama University.

Bromination of 1a with NBS. *a) In DMF.* A solution of 5.52 g (31 mmol) of NBS in 70 ml of DMF was added to a stirred and ice-cooled solution of 5.05 g (30 mmol) of **1a** in 50 ml of DMF. After stirring for 3 h under ice-cooling, ice-water (*ca.* 150 ml) was added and the resulting mixture was extracted with CH_2Cl_2 (60 ml x 3). The extracts were washed with water, dried over anhydrous magnesium sulfate, and evaporated. The residue was subjected to silica-gel column chromatography (*ca.* 400 g). Elution with hexane gave 0.93 g (9.5%) of 2,5-dibromo-3,6-dimethylthieno[3,2-*b*]thiophene (**3a**), 5.99 g (81%) of 2-bromo-3,6-dimethylthieno[3,2-*b*]thiophene (**2a**), and 0.34 g (7%) of **1a** in this order. **2a**: m.p. 47.5-48 °C (from MeOH); ^1H NMR δ 2.22 (s, 3H), 2.25 (d, $J = 0.9$ Hz, 3H), 6.89 (q-like, 1H); ^{13}C NMR δ 13.99, 14.49, 109.64, 120.77, 128.23, 129.87, 137.70, 138.29. Anal. Calcd. for $C_8H_7BrS_2$: C, 38.87; H, 2.85. Found: 38.59; H, 2.85. **3a**: m.p. 143-144 °C (from hexane); ^1H NMR δ 2.24 (s); ^{13}C NMR δ 14.09, 109.71, 129.72; 136.48. Anal. Calcd. for $C_8H_6Br_2S_2$: C, 29.47; H, 1.85. Found: C, 29.50; H, 1.85.

b) In a mixture of CH_2Cl_2 and AcOH. A solution of 538 mg (3 mmol) of NBS in 15 ml of CH_2Cl_2 was added to a stirred and ice-cooled solution of 507 mg (3 mmol) of **1a** in 20 ml of CH_2Cl_2/AcOH (7:3). After stirring for 3 h under ice-cooling, the mixture was purified as described above to give 497 mg (66%) of **2a**, 107 mg (11%) of **3a**, and 57 mg (11%) of **1a**.

Chlorination of 1a (840 mg, 5 mmol) with NCS (667 mg, 5 mmol) in DMF followed by purification on a column of silica gel gave 130 mg (11%) of 2,5-dichloro-3,6-dimethylthieno[3,2-*b*]thiophene (**3c**), 780 mg (77%) of 2-chloro-3,6-dimethylthieno[3,2-*b*]thiophene (**2c**), and 50 mg (6%) of **1a** in this order. **2c**: m.p. 44-45 °C (from MeOH); ^1H NMR δ 2.21 (s, 3H), 2.22 (d, 3H), 6.83 (m, 1H). Anal. Calcd. for $C_8H_7ClS_2$; C, 47.40; H, 3.48. Found: C, 47.22; H, 3.45. **3c**: m.p. 127-128 °C (from hexane); ^1H NMR δ 2.22 (s). Anal. Calcd. for $C_8H_6Cl_2S_2$; C, 40.51; H, 2.55. Found: C, 40.44; H, 2.55.

Bromination of 1b (786 mg, 3 mmol) with NBS (625 mg, 3.5 mmol) in DMF followed by purification on a column of silica gel gave 218 mg (17%) of 2,5-dibromo-3,6-dimethylselenolo[3,2-*b*]selenophene (**3b**) and 789 mg (77%) of 2-bromo-3,6-dimethylselenolo[3,2-*b*]selenophene (**2b**). **2b**: m.p. 53.5-54 °C (from isopropanol); ^1H NMR δ 2.27 (s, 3H), 2.29 (d, $J = 0.8$ Hz, 3H), 7.51 (q-like, 1H); ^{13}C NMR δ 16.35, 17.15, 109.44, 123.09, 134.84, 134.98, 139.79, 139.81. Anal. Calcd. for $C_8H_7BrSe_2$: C, 28.18; H, 2.07. Found: C, 27.99; H, 2.09. **3b**: m.p. 151.5-152 °C (from hexane); ^1H NMR δ 2.20 (s); ^{13}C

NMR δ 16.34, 110.01, 134.66, 138.31. Anal. Calcd. for $C_8H_6Br_2Se_2$: C, 22.89; H, 1.44. Found: C, 22.81; H, 1.39.

Preparation of 2,2'-Bi[3,6-dimethylthieno[3,2-*b*]thiophene] (4a) from 2a. A mixture of 197 mg (1.52 mmol) of anhydrous nickel(II) chloride, 3.05 g (46.6 mmol) of zinc powder, 3.00 g (11.4 mmol) of triphenylphosphine, and 1.55 g (15.0 mmol) of sodium bromide in 50 ml of DMF was heated at 50 °C for 30 min under argon. To the resulting reddish brown mixture was added a solution of 1.86 g (7.53 mmol) of the bromothienothiophene **2a** in 25 ml of DMF. The mixture was heated at 62-70 °C for 4 h, cooled to room temperature, and diluted with water. The resulting precipitate was collected by filtration and then stirred with CH_2Cl_2 (100 ml), and the insoluble material was removed. The filtrate was dried over anhydrous magnesium sulfate and evaporated. The residue was subjected to silica-gel column chromatography (*ca.* 150 g). Elution with hexane gave 118 mg (9%) of **1a** and then 629 mg (50%) of **4a**: m.p. 174-175 °C (from hexane); pale-yellow plates; ^{1}H NMR δ 2.30 (s, 6H), 2.37 (d, J = 1.3 Hz, 6H), 6.97 (q-like, 2H); ^{13}C NMR δ 13.82, 14.75, 121.60, 129.71, 130.23, 130.95, 139.16, 140.47; *m/z* 334 (M^+); λ_{max} (CH_2Cl_2) (log ε) 265 (4.19), 277 (4.22), 286 nm (4.17). Anal. Calcd for $C_{16}H_{14}S_4$: C, 57.44; H, 4.22. Found: C, 57.35; H, 4.24.

Preparation of 2,2'-Bi[3,6-dimethylselenolo[3,2-*b*]selenophene] (4b). *a) By reductive coupling of* ***2b****.* The bromoselenoloselenophene **2b** (1.36 g, 4.0 mmol) was heated with the nickel reagent, prepared from 104 mg (0.8 mmol) of nickel(II) chloride, 1.59 g (6.0 mmol) of triphenylphosphine, 1.62 g (25 mmol) of zinc powder, and 823 mg (8 mmol) of sodium bromide, in DMF (35 ml) at 62-70 °C for 6 h under argon. The resulting mixture was purified as described above to give 384 mg (37%) of **1b** and 24 mg (2%) of **4b**; m.p. 235.5-236.5 °C (from hexane); pale-yellow plates; ^{1}H NMR δ 2.26 (s, 6H), 2.35 (d, J = 1.1 Hz, 6H), 7.48 (q-like, 2H); ^{13}C NMR δ 15.98, 17.39, 123.50, 133.54, 135.31, 135.61, 141.34, 142.28; *m/z* 526 (M^+); λ_{max} (CH_2Cl_2) (log ε) 291 (4.30), 318 (4.55), 337 nm (4.39). Anal. Calcd for $C_{16}H_{14}Se_4$: C, 36.81; H, 2.70. Found: C, 37.04; H, 2.65.

b) By Pd(PPh$_3$)$_4$-catalyzed coupling of ***2b*** *with the Grignard reagent* ***5b'****.* To a solution of 2.62 g (10 mmol) of **1b** in 35 ml of ether, cooled by an ice-salt bath, was added 6.7 ml of a 1.64 M hexane solution of butyllithium (11 mmol). The mixture was stirred for 1 h under ice-cooling. To this mixture, was added magnesium bromide, which was prepared from 2.44 g (13 mmol) of 1,2-dibromoethane and 292 mg (12 mmol) of magnesium in 35 ml of ether. The resulting mixture containing **5b'** was added to a stirred and ice-cooled mixture of 1.71 g (5.0 mmol) of **2b** and 290 mg (0.025 mmol) of $Pd(PPh_3)_4$ in 40 ml of ether under ice-cooling. The mixture was warmed to room temperature and refluxed for 24 h under argon to give a mixture containing yellow precipitates. Ice-water was added to the mixture, and the insoluble solid was collected by filtration and washed with water, methanol (20 ml), and ether (50 ml) to give 2.20 g (85%) of the crude **4b**. The filtrate and washings were combined, washed with water, dried, and evaporated. The residue was chromatographed on a column of silica gel and eluted with hexane to give 20 mg of **4b**, 150 mg of **2b**, and 1.23 g of **1b**.

c) By NiCl$_2$(dppp)-catalyzed coupling of ***2b*** *with* ***5b'****.* The Grignard reagent **5b'**, prepared from 2.10 g (8 mmol) of **1b** in the same manner as described above, and 680 mg (2 mmol) of **2b** were refluxed in ether for 24 h in the presence of 113 mg of $NiCl_2$(dppp) under argon. After addition of ice-water, the mixture was extracted with CH_2Cl_2 (30 ml x 3) and the extracts were washed with water, dried over magnesium sulfate, and evaporated. The residue was chromatographed on a column of silica gel (100 g). Elution with hexane gave 491 mg of **2b**, 991 mg of **1b**, 188 mg (18%) of the expected **4b**.

d) By $NiCl_2(dppp)$-catalyzed coupling of ***2b*** *with* ***5b****.* The lithiated selenoloselenophene **5b**, prepared from 2.10 g (8 mmol) of **1b**, and 682 mg (2 mmol) of **2b** were refluxed in ether for 24 h in the presence of 150 mg of $NiCl_2$(dppp) under argon. Chromatographic purification of the mixture gave 361 mg of **2b**, 863 mg of **1b**, and 220 mg (21%) of **4b**.

2,5-Dibromo-3,6-dimethylthieno[3,2-*b*]thiophene (3a). A solution of 2.14 g (12 mmol) of NBS in 40 ml of CH_2Cl_2 was added to a stirred solution of 0.84 g (5 mmol) of **1a** in 25 ml of CH_2Cl_2/AcOH (7:3). The mixture was stirred for 3 h, washed with 10% aqueous $NaHCO_3$ and then with water, dried over anhydrous magnesium sulfate, and evaporated. The residue was recrystallized from hexane to give 1.52 g (93%) of **3a**, m.p. 143-144 °C.

2,5-Dibromo-3,6-dimethylselenolo[3,2-*b*]selenophene (3b), (1.93 g, 92%), m.p. 151.5-152 °C, was prepared from 1.31 g (5 mmol) of **1b** and 2.14 g (12 mmol) of NBS in 92% yield in the same way as described above.

Preparation of 2,2':5,'2"-Ter[3,6-dimethylthieno[3,2-*b*]thiophene] (7a). *a) Attempted synthesis from* ***5a*** *and* ***3a****.* A 1.61 M hexane solution of butyllithium (1.25 ml, 2 mmol) was added to a solution of **1a** (336 mg, 2 mmol) in 12 ml of ether cooled by an ice-salt bath. The mixture was stirred for 2 h under cooling, warmed to room temperature, and stirred for 0.5 h (quenching of the mixture with D_2O at this stage followed by ^1H NMR analysis revealed that the lithiation took place nearly quantitatively). The resulting mixture containing **5a** was added to a solution of 326 mg (1 mmol) of **3a** and 50 mg (0.08 mmol) of $NiCl_2(PPh_3)_2$ in 30 ml of ether. The mixture was refluxed for 8 h under argon, cooled to room temperature, and quenched by addition of ice-water (*ca.* 50 ml). CH_2Cl_2 (50 ml) was added to this mixture and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (30 ml x 2). The extracts were combined, washed with water, dried over anhydrous magnesium sulfate, and evaporated. The residue was chromatographed on a column of silica gel (100 g). Elution with hexane gave 23 mg (7%) of **3a**, 207 mg (84%) of **2a**, 34 mg (10%) of **1a**, 11 mg of 2-bromo-5,2'-bi[3,6-dimethylthieno[3,2-*b*]thiophene] (3%) (**6a**), 59 mg (18%) of **4a** in this order. **6a**: m.p. 161-162 °C (from hexane); pale-yellow needles; ^1H NMR (200 MHz) δ 2.30 (s, 3H), 2.32 (s, 3H), 2.33 (s, 3H), 2.40 (s, 3H), 7.02 (s, 1H); ^{13}C NMR (50 MHz) δ 13.77, 13.81, 14.18, 14.73, 110.00, 121.76, 129.26, 129.90, 129.93, 130.15, 130.25, 130.31, 137.78, 138.39, 139.31, 140.54; *m/z* 412, 414 (M^+). Anal. Calcd for $C_{16}H_{13}BrS_4$: C, 46.48; H, 3.17. Found: C, 46.64; H, 3.12.

b) $NiCl_2(PPh_3)_2$-catalyzed synthesis of ***7a*** *from* ***5a'*** *and* ***3a****.* Thienothiophene **1a** (4 mmol) was lithiated with butyllithium (4 mmol) in 12 ml of ether in the same manner as described above. To this mixture containing **5a** was added magnesium bromide, prepared from 752 mg (4 mmol) of 1,2-dibromoethane and 99 mg (4 mmol) of magnesium in 15 ml of ether, under ice-cooling. The mixture was stirred for 2 h under ice-cooling. The resulting mixture containing the Grignard reagent **5a'** was added to a solution of 326 mg (1 mmol) of **3a** and 53 mg (0.1 mmol) of $NiCl_2(PPh_3)_2$ in 20 ml of ether under ice-cooling. The mixture was warmed to room temperature and then refluxed for 8 h under argon. The reaction was quenched by addition of ice-water and the resulting precipitate was collected by filtration and air-dried. The filtrate was extracted with CH_2Cl_2 and the extracts were washed with water, dried, and evaporated. The solid material obtained from the original mixture and the residue obtained by CH_2Cl_2 extraction were combined and subjected to silica-gel column chromatography (120 g). Elution with hexane gave 110 mg (34%) of **3a**, 210 mg (31%) of **1a**, 88 mg (21%) of **6a**, 115 mg (35%) of **4a**, and 49 mg (10%) of **7a** in this order. **7a**: m.p. 281-282 °C (dec) (from toluene); pale-yellow granules; ^{1}H NMR (400 MHz) δ 2.325 (s, 6H), 2.329 (s, 6H), 2.39 (s, 6H), 7.01 (broad s, 2H); ^{13}C NMR (100 MHz) δ 13.88, 13.95, 14.79, 121.73, 129.55, 129.88, 130.30, 130.73, 130.90, 139.19, 139.69, 140.56; *m/z* 500 (M^+); UV-Vis (CH_2Cl_2) λ_{max} (log ε) 263 (4.20), 298 (4.36), 337 nm (4.50). Anal. Calcd for $C_{24}H_{20}S_6$: C, 57.56; H, 4.03. Found: C, 56.83; H, 3.98.

c) $NiCl_2(dppp)$-catalyzed synthesis of ***7a*** *from* ***5a'*** *and* ***3a***. This reaction was carried out on the same scale and in the same way as described above except that 53 mg (0.1 mmol) of $NiCl_2(dppp)$ was used instead of $NiCl_2(PPh_3)_2$. Chromatographic purification of the mixture gave 69 mg (21%) of **3a**, 244 mg (36%) of **1a**, 61 mg (15%) of **6a**, 102 mg (31%) of **4a**, and 209 mg (42%) of **7a**.

Preparation of 2,2':5',2"-Ter[3,6-dimethylselenolo[3,2-*b*]selenophene] (7b). *a) $Pd(PPh_3)_4$-catalyzed coupling of* ***2b*** *and* ***8b'***. To a solution of 1.14 g (2.7 mmol) of the dibromoselenoloselenophene **3b** in 30 ml of THF was added, under cooling by an ice-salt bath, 3.5 ml (5.8 mmol) of 1.66 M hexane solution of butyllithium. The mixture was stirred for 2 h at 0 °C. To this mixture was added under ice-cooling zinc bromide, prepared by heating 490 mg (7.5 mmol) of zinc powder and 1.45 g (7.7 mmol) of 1,2-dibromoethane in 30 ml of refluxing THF. The mixture containing a yellow solid precipitate, on stirring for 2 h at 0 °C, turned to a transparent yellow solution, which was added to a solution of 1.72 g (5 mmol) of **2b** and 231 mg (0.2 mmol) of $Ph(PPh_3)_4$ in 15 ml of THF. The mixture was warmed slowly and then refluxed for 24 h under argon. The reaction was quenched by addition of ice-water (50 ml) and the resulting solid precipitate was collected by filtration and washed with water, methanol (50 ml), and ether (40 ml) to give 600 mg (31%) of practically pure **7b**. CH_2Cl_2 (100 ml) was added to the filtrate and washings combined. The organic layer was washed with water, dried over magnesium sulfate, and evaporated. The residue was chromatographed on a column of silica gel (150 g). Elution with hexane gave 887 mg (52%) of **2b**, a trace amount of 5-bromo-2,2'-bi-3,6-dimethylselenolo[3,2-*b*]selenophene (**6b**) (spectroscopic data of this compound will be given later), 102 mg (14%) of **1b**, and 411 mg (16%) of **4b**. **7b**: m.p. 332-334 °C (dec) (from *o*-xylene); orange powder; ^{1}H NMR (400 MHz) δ 2.27 (s, 6H), 2.28 (s, 6H), 2.35 (d, *J* = 0.9 Hz, 6H), 7.50 (q-like, 2H); ^{13}C NMR (100 MHz) δ 16.03, 16.14, 17.37, 123.62, 133.63, 133.84, 135.43, 135.46, 135.72, 141.62, 142.23, 142.48; λ_{max} (log ε) (CH_2Cl_2) 291 (4.40), 322 (4.57), 357 nm (4.59). Anal. Calcd for $C_{24}H_{20}Se_6$: C, 36.85; H, 2.58. Found: C, 37.11; H, 2.55.

b) *$NiCl_2(dppp)$-catalyzed coupling of* ***3b*** *with the Grignard reagent* ***5b'*** did not give any amount of the trimer **7b**. The reaction gave trace amounts of **4b** and **6b** in addition to **1b** and **3b**.

c) *$NiCl_2(dppp)$-catalyzed coupling of* ***2b*** *with the dilithium salt* ***8b*** gave the trimer **7b** in low yield (1.4%) in addition to **4b** (7%), **2b** (56%) and **1b** (29%).

Bromination of 4a (493 mg, 1.5 mmol) with 1 **equimolar amount of NBS** in DMF followed by purification on a column of silica gel gave 161 mg (22%) of 5,2'-bi[2-bromo-3,6-dimethylthieno[3,2-*b*]thiophene] (**9a**), 368 mg (60%) of **6a**, and 62 mg (13%) of **4a**. **9a**: m.p. 200-202 °C (from $CHCl_3$/hexane);

^{1}H NMR (200 MHz) δ 2.25 (s, 6H), 2.30 (s, 6H); ^{13}C NMR (50 MHz) δ 13.78, 14.19, 110.20, 111.09, 129.49, 129.94, 137.94, 138.46. Anal. Calcd for $C_{16}H_{12}Br_2S_4$: C, 39.03; H, 2.46. Found: C, 39.28; H, 2.41.

Bromination of 4a (748 mg, 4.2 mmol) with **2 equimolar amounts of NBS** in $AcOH/CH_2Cl_2$ followed by recrystallization from $CHCl_3$/hexane gave 906 mg (92%) of **9a**, m.p. 200-202 °C.

Preparation of 5,2':2',2":5",2"'-Quater[3,6-dimethylthieno[3,2-*b*]thiophene] (10a). *a) By coupling of the dibromide **9a** with the Grignard reagent **5a'**.* A solution of 344 mg (0.7 mmol) of the dibromide **9a** in 20 ml and a solution of the Grignard reagent **5a'** in 30 ml of ether (prepared from 940 mg (5.6 mmol) of **1a**) were combined and heated at reflux in the presence of 52 mg (0.11 mmol) of $NiCl_2$(dppp) under argon for 48 h. The reaction was quenched by addition of 50 ml of ice-water. The resulting precipitate was collected by filtration and washed with water and methanol (15 ml). The filtrate and washings were combined, washed with water, dried over anhydrous magnesium sulfate, and evaporated. The precipitate and the residue were combined and chromatographed on a column of silica gel (120 g). Elution with hexane gave 592 mg (63%) of **1a**, 106 mg (31%) of **6a**, 195 mg (48%) of a compound considered to be the monobromide **11a** of the trimer **7a**, and 11 mg (2.3%) of the tetramer **10a**. **10a**: m.p. 356-360 °C (dec); mud yellow powder (from chlorobenzene); ^{1}H NMR (400 MHz) δ 2.33 (s, 12H), 2.35 (s, 6H), 2.38 (s, 6H), 7.00 (broad s, 2H); *m/z* 666 (M^+). Anal. Calcd for $C_{32}H_{26}S_8$: C, 57.62; H, 3.93. Found: C, 57.38; H, 3.94.

*b) By coupling of the bromide **6a** with the Grignard reagent **12a**.* To a solution of 924 mg (2.8 mmol) of **4a** in ether (35 ml) was added 1.8 ml (2.9 mmol) of 1.61 M hexane solution of butyllithium under cooling an ice-salt bath. The mixture was warmed to 0 °C during 2 h (in a separate experiment, quenching with D_2O at this stage revealed that the lithiation took place more than in 90% yield). To this solution was added a solution of $MgBr_2$ prepared from 1,2-dibromoethane (3.6 mmol) and magnesium (3.5 mmol) in ether (15 ml) under ice-cooling and the mixture was stirred for 2 h. The resulting mixture was added to a solution of 289 mg (0.7 mmol) of the bromide **6a** and 27 mg (0.05 mmol) of $NiCl_2$(dppp) in ether (20 ml) and heated at reflux for 50 h under argon. After the reaction was quenched by addition of 50 ml of ice-water, the resulting precipitate was collected by filtration and washed with water and methanol (20 ml). The filtrate and the washings were combined, washed with water, dried over anhydrous magnesium sulfate, and evaporated. The precipitate and the residue were combined and chromatographed on a column of silica gel (100 g). Elution with hexane gave **6a** in a trace amount and then 463 mg (50%) of **4a**. Finally the column was eluted with benzene/CH_2Cl_2 (4:1) to give 392 mg (84%) of **10a**, m.p. 356-360 °C.

Bromination of 4b (835 mg, 1.6 mmol) with 1 equimolar amount of NBS in DMF gave 257 mg (24%) of 2,2'-bi[2-bromo-3,6-dimethylselenolo[3,2-*b*]selenophene] (**9b**), 549 mg (57%) of 5-bromo-2,2'-bi[3,6-dimethylselenolo[3,2-*b*]selenophene (**6b**), and 125 mg (15%) of **4b**. **6b**: m.p. 196-197 °C (from hexane); ^{1}H NMR (200 MHz) δ 2.22 (s, 3H), 2.26 (s, 3H), 2.29 (3, 3H), 2.36 (d, J =1.1 Hz, 3H), 7.51 (q-like, 1H); ^{13}C NMR (50 MHz) δ 15.94, 15.99, 16.51, 17.38, 109.93, 123.65, 133.04, 133.77, 134.75, 135.00, 135.30, 135.33, 139.81, 140.56, 141.47, 142.32. Anal. Calcd for $C_{16}H_{13}BrSe_4$: C, 31.98; H, 2.18. Found: C, 32.00; H, 2.13. **9b**: m.p. > 168 °C (dec) (from CH_2Cl_2/hexane); ^{1}H NMR (200 MHz) δ 2.20 (s, 6H), 2.28 (s, 6H); ^{13}C NMR (50 MHz) δ 15.95, 16.51, 110.13, 111.19, 133.31, 134.49, 134.52, 135.02. Anal. Calcd for $C_{16}H_{12}Br_2Se_4$: C, 28.27; H, 1.78. Found: C, 28.43; H, 1.76.

Preparation of 2,2':5',2":5",2"'-Quater[3,6-dimethylselenolo[3,2-*b*]selenophene] (10b). To a solution of 732 mg (1.4 mmol) of the dimer **4b** in ether (25 ml) was added 1.0 ml (1.6 mmol) of 1.64 M hexane solution of butyllithium under cooling by an ice-salt bath. The mixture was warmed to 0 °C during 2 h (in a separate experiment, quenching the lithiation with D_2O at this stage revealed that **4b** was lithiated more than in 90% yield). To this solution was added $MgBr_2$ prepared from 1,2-dibromoethane (2.2 mmol) and magnesium (2.0 mmol) in ether (12 ml) under ice-cooling and the mixture was stirred for 2 h. The Grignard reagent solution thus obtained and a solution of 361 mg (0.6 mmol) of the bromide **6b** in ether (35 ml) were combined and heated at reflux in the presence of 35 mg (0.03 mmol) of $Pd(PPh_3)_4$ for 50 h under argon. The reaction was quenched by addition of water and the resulting precipitate was collected by filtration, washed with water, methanol (15 ml), and THF (20 ml), and then recrystallized from *o*-chlorotoluene to give 257 mg (41%) of the tetramer **10b**: m.p. > 400 °C (dec); ^{1}H NMR (400 MHz) δ 2.28 (s, 6H), 2.29 (s, 6H), 2.35 (s, 6H), 2.37 (s, 6H), 7.51 (broad s, 2H). Elemental analysis of this compound did not give satisfactory results probably because of the inclusion of the solvent molecule (*o*-chlorotoluene) of recrystallization, even after dried at 50 °C under vacuum for 24 h; Anal. Calcd for $C_{32}H_{26}Se_8$: C, 36.88; H, 2.51. Found: C, 37.97; H, 2.57.

X-Ray Crystal Structure Determination; *crystal data*; $C_{16}H_{14}Se_4$, M_r = 522.00, monoclinic, $P2_1/n$, a = 9.189(3), b = 6.912(4), c = 26.347(14) Å, β = 93.78(2)°, V = 1669.8 Å^3, Z = 4, D_{calc} = 2.076 gcm^{-3}, μ(Mo $K\alpha$) = 8.689 mm^{-1}.

A pale yellow crystal with dimensions 0.34 x 0.20 x 0.20 mm was mounted on a Mac Science DIP3000 diffractometer equipped with a graphite monochrometer. Oscillation and nonscreen Weissenburg photographs were recorded on the imaging plates of the diffractometer by using Mo $K\alpha$ radiation (λ = 0.71073 Å) and the data reduction was made by the MAC-DENZO program system. Intensity data of 4311 unique reflections were collected in the range of $0 \leq h \leq 11$, $0 \leq k \leq 9$, and $-37 \leq l \leq 37$. Cell parameters were determined and refined by using the MAC-DENZO for all observed reflections. The structure was solved by direct methods using SIR[17] in the CRYSTAN-GM program system. The atomic coordinates and anisotropic thermal parameters of the non-H atoms were refined by full-matrix least squares[18] to minimize the functions, $\Sigma(|F_O|-|F_C|)^2$, for 2861 reflections with $|F_O| > 3\sigma(|F_O|)$. The final R and $R\omega$ values are 0.076 and 0.098, respectively. The final positional and thermal parameters of non-H atoms are listed in Table 3. Structure determination and refinements were made by using the CRYSTAN-GM program system. All the calculations were carried out on a SUN SPARC 10 workstation.

Table 3. Atomic Coordinates and Equivalent Thermal Parameters

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq} (A^3)
Se (1)	0.81296 (19)	-0.20211 (26)	-0.05389 (5)	0.049
Se (2)	0.72430 (18)	0.17176 (23)	0.07627 (5)	0.043
Se (3)	1.03325 (17)	0.12945 (23)	0.18195 (5)	0.041
Se (4)	0.9315 (2)	0.3207 (3)	0.2926 (1)	0.052
C (1)	0.6850 (19)	0.0033 (25)	-0.0754 (5)	0.054
C (2)	0.6534 (15)	0.1189 (24)	-0.0369 (5)	0.043
C (3)	0.7256 (15)	0.0679 (21)	0.0101 (4)	0.036
C (4)	0.8122 (18)	-0.0970 (22)	0.0118 (4)	0.044
C (5)	0.8824 (15)	-0.1569 (21)	0.0589 (5)	0.038
C (6)	0.8502 (15)	-0.0335 (22)	0.0978 (5)	0.040
C (7)	0.8995 (14)	-0.0545 (21)	0.1514 (4)	0.034
C (8)	0.8646 (16)	-0.1954 (21)	0.1840 (5)	0.040
C (9)	0.9362 (16)	-0.1719 (20)	0.2333 (5)	0.038
C (10)	1.0281 (15)	-0.0209 (22)	0.2417 (5)	0.039
C (11)	1.1036 (15)	0.0000 (24)	0.2908 (5)	0.043
C (12)	1.0680 (16)	-0.1396 (22)	0.3228 (5)	0.043
C (13)	0.557 (2)	0.298 (3)	-0.043 (1)	0.072
C (14)	0.9800 (17)	-0.3305 (23)	0.0640 (6)	0.048
C (15)	0.7640 (18)	-0.3584 (27)	0.1710 (6)	0.055
C (16)	1.208 (2)	0.160 (3)	0.304 (1)	0.070

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