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Novel Thiophene Oligomers Containing a Redox Active Hexaarylethane Unit

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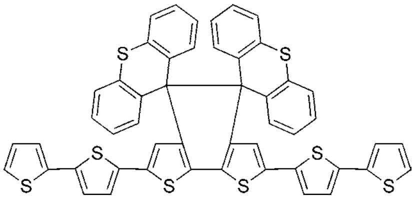
ABSTRACT



Novel thiophene oligomers containing a redox active hexaarylethane unit have been prepared as a new class of molecular wires having a large electrochemical bistability and definitely characterized by using single-crystal X-ray structure analysis and redox potential measurements. They constitute reversible redox pairs with the corresponding bis(thioxanthyl) dications by undergoing C–C bond making/breaking. They show unique electrochromism and a fluorescence change during interconversion.

Thiophene oligomers are one of the most important materials for making molecular nanowires[1] because of their excellent electron and energy transfer properties through the π-conjugation, which can be utilized for the fabrication of molecular devices.[2] On the other hand, switching such molecular wires by external stimuli is an important theme. For this purpose, switching of the π-conjugation using a conformational change has been considered. Among thiophene oligomers, for example, 1,2-dithienylcyclopentene derivatives have been reported as electro-photochromic compounds showing a switching function, where two stable forms can be exchanged by light or electron transfer.[3] However, oligothiophenes undergoing a drastic molecular motion leading to a large electrochemical bistability[4] are still rare. In this context, we have now designed oligothiophenes containing a hexaarylethane unit, which constitute reversible redox pairs with bis(triarylmethylenium)-type dications as shown in Figure 1. In this system, oxidation of the oligothiophene unit induces the C−C bond breaking of the hexaarylethane bond accompanied by the generation of highly colored triaryl-

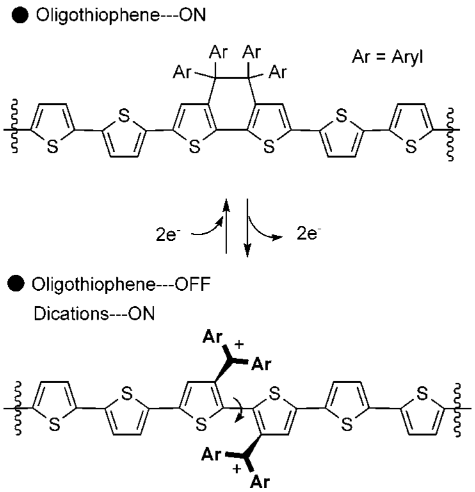


Figure 1. Model of a thiophene wire incorporating a redox active unit.

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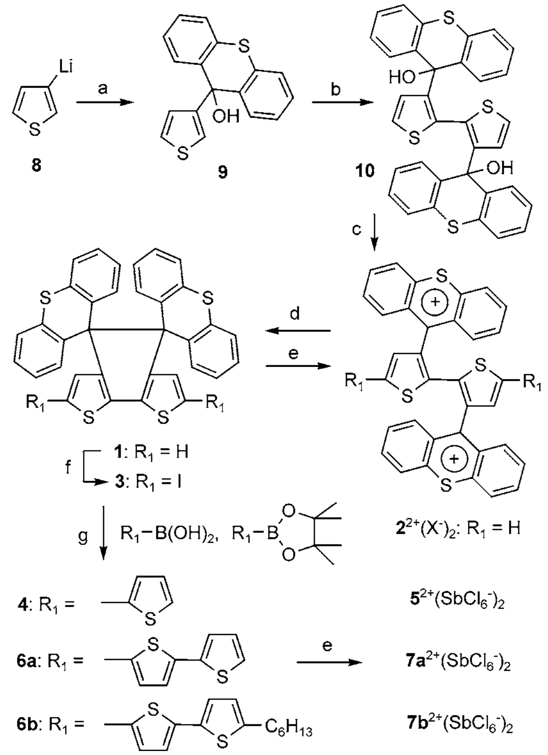
methylenium ions. Oligothiophene units should adopt a twist conformation as a result of the Coulomb repulsion between the two triarylmethylenium units (oligothiophene OFF state). On the other hand, reduction of the cations regenerates the normal oligothiophene π-conjugation (oligothiophene ON state). During this interconversion, the properties of oligothiophenes are considered to be drastically changed with unique color and fluorescence changes.[5] Although oligothiophenes are known as electrochromic materials,[6] the derivatives incorporating other strong chromophors are rare. Such systems are expected to exhibit multicolored electrochromism. Moreover, these compounds possess reactive terminal α-positions of thiophene units, where other functional groups can be introduced. Unique electron-transfer devices might be constructed by connecting them with electron acceptor parts.[2] We report here the preparation, properties, and structure of such unique thiophene oligomers.

Scheme 1 ^{a}

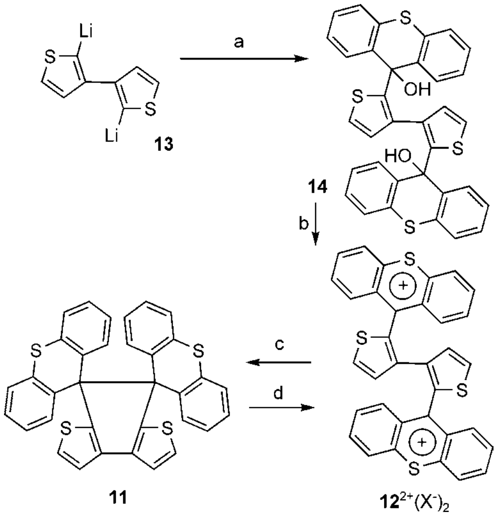


^{a} Reagents: (a) thioxanthone, 77%; (b) *n*-BuLi, CuCl$_2$, 34%; (c) HBF$_4$, **2**$^{2+}$(BF$_4^-$)$_2$, 94%; (d) Zn, 89%; (e) (p-BrC$_6$H$_4$)$_3$N$^{+\cdot}$SbCl$_6^-$; **2**$^{2+}$(SbCl$_6^-$)$_2$, 94%, **5**$^{2+}$(SbCl$_6^-$)$_2$, 93%, **7a**$^{2+}$(SbCl$_6^-$)$_2$, 52%, **7b**$^{2+}$(SbCl$_6^-$)$_2$, 88%, (f) *n*-BuLi, ICH$_2$CH$_2$I, 84%; (g) Pd(PPh$_3$)$_4$; **4**, 64%; **6a**, 28%; **6b**, 84%.

9-Hydroxy-9-(3-thienyl)thioxanthene **9** was prepared by the reaction of 3-lithiothiophene **8** with thioxanthone in ether at −78 °C. Lithiation of this alcohol **9** by 2 equiv of *n*-butyllithium followed by oxidation with CuCl$_2$ afforded diol **10** in high yield. Bis(thioxanthylium)-type dication **2**$^{2+}$(BF$_4^-$)$_2$ was obtained by treating diol **10** with HBF$_4$ in acetic anhydride. Reduction with Zn of dication salt **2**$^{2+}$(BF$_4^-$)$_2$ formed a C−C bond between the methylenium carbons to afford bithiophene-type hexaarylethane **1**. Dilithiation of **1** with *n*-butyllithium followed by reaction with diiodoethane afforded diiodohexaarylethane **3** in good yield. A Suzuki coupling of **3** with the corresponding thiophene-2-boric acids or a thiophen-2-yl-dioxaborolane (for **6a**) gave a quaterthiophene derivative **4** and sexithiophenes **6a**,**b**. Oxidation of hexaarylethane **1** with 2 equiv of (p-BrC$_6$H$_4$)$_3$N$^{+\bullet}$SbCl$_6^-$ led to fission of the C−C bond to regenerate the dication **2**$^{2+}$, which was isolated as SbCl$_6^-$ salt in excellent yield. The efficient interconversion between bithiophene-hexaarylethane **1** and **2**$^{2+}$ indicates that they constitute a "reversible" redox pair undergoing bond making/breaking upon electron transfer. On the other hand, the similar oxidation of quaterthiophene **4** and sexithiophenes **6a**,**b** afforded the corresponding dications **5**,**7a**,**b**$^{2+}$(SbCl$_6^-$)$_2$ as stable solids in good yields. Oxidation of sexithiophene derivative **6a** having no alkyl groups at α,ω-positions was carefully conducted because a polymerization reaction of the oligothiophene competed with the bond cleavage reaction as described later.

3,3′-Bithiophene-type hexaarylethane **11** and dication **12**$^{2+}$ were prepared for comparisons according to the procedure shown in Scheme 2. They also constitute reversible redox pairs.

Scheme 2 ^{a}



^{a} Reagents: (a) thioxanthone, 40%; (b) HBF$_4$, **12**$^{2+}$(BF$_4^-$)$_2$, 94%; (c) Zn, 97%; (d) (p-BrC$_6$H$_4$)$_3$N$^{+\cdot}$SbCl$_6^-$, **12**$^{2+}$(SbCl$_6^-$)$_2$, 92%.

The structure of **6a** was revealed by X-ray analysis.[7] Two crystallographically independent molecules exist (molecule

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1 and molecule 2). The structure of molecule 1 is shown in Figure 2a. The ethane bond is unusually long [1.655(5) Å in molecule 1 and 1.673(5) Å in molecule 2] compared with a standard C−C bond length (1.54 Å). Such a long bond length is also observed in a related 3,3′-bithiophene derivative **11** [1.656(5)−1.679(5) Å]. This elongation of the C−C bond seems to be caused by the steric effect of the aryl groups.[8] The molecule **6a** is thermally stable in air (mp 379−380 °C), indicating that these long bonds are difficult to be homolytically cleaved. The dihedral angles of the central bithiophene moieties are only 1.4° and 5.7°. The oligothiophene residues are also planar and adopt transoid conformation. This result shows the efficient π-conjugation in the oligothiophene skelton **6a**. On the other hand, the structure of the dication was investigated by X-ray analysis of dication $\mathbf{12}^{2+}(\mathrm{SbCl_6}^-)_2$ (Figure 2b). The distance between the two cation carbons is 5.34 Å, and the dihedral angle of the bithiophene unit is 143.7°, which is much larger than those of the corresponding biphenyl- and binaphthyl-type dications (69.2−73.0°),[4c,5] suggesting the easier free rotation around the bithiophene axis.

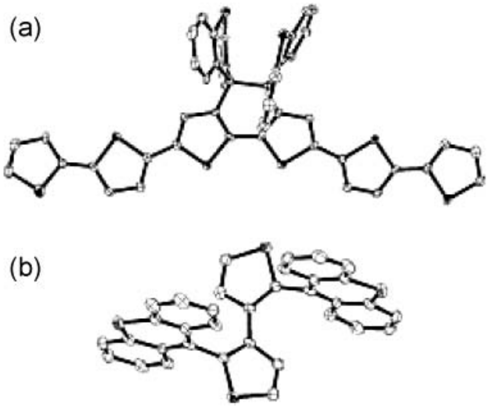

Figure 2. Molecular structures of sexithiophene **6a** (Molecule 1) (a) and dication $\mathbf{12}^{2+}(\mathrm{SbCl_6}^-)_2$ (b). Counteranions of $\mathrm{SbCl_6}$ and included MeCN molecules are omitted for clarity.

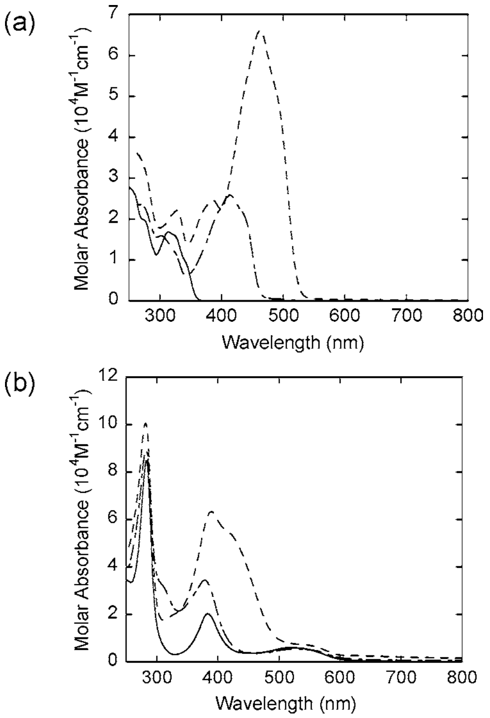

Figure 3. Absorption spectra of (a) oligothiophenes containing a hexaarylethane **1** (solid line), **4** (dashed line), and **6b** (dotted line), and (b) bis(thioxanthyl) dications $\mathbf{2}^{2+}$ (solid line), $\mathbf{5}^{2+}$ (dashed line), and $\mathbf{7b}^{2+}$ (dotted line).

Hexaarylethane **1** is a colorless compound. The absorption maxima of **4** and **6** are shifted to longer wavelengths with an increase in the number of thienyl units as shown in Figure 3a. On the other hand, sexithiophene derivatives **6a,b** show efficient fluorescence at 516 nm (quantum yield; $\Phi = 0.30$) and 520 nm ($\Phi = 0.25$), respectively. In contrast, the dication states $\mathbf{7a,b}^{2+}$ did not exhibit any fluorescence. This result indicates that the present system works as a novel redox-fluorescence switch. The absorption maximum of sexithiophene **6b** at 463 nm was shifted to 389 nm and a new absorption at 520 nm attributed to thioxanthylium units that appeared (Figure 3b). These absorptions are observed commonly in dication $\mathbf{2,5,7a}^{2+}$ and are summarized in Table 1. This result suggests that a unique electrochromic system is realized by using these redox couples. The fact that the absorptions of the sexithiophene unit in **6a**,**b** are shifted to shorter wave-

Table 1. UV−vis and Fluorescence Data

compound	$\lambda_{\max}^{\mathrm{abs}}$ (nm (log ϵ))	$\lambda_{\max}^{\mathrm{emis}}$ (nm) (Φ_f)^c
1	312 (4.20)^a	
$\mathbf{2}^{2+}(\mathrm{BF_4}^-)_2$	384 (4.31), 520 (3.77)^b	
4	413 (4.41)^a	
$\mathbf{5}^{2+}(\mathrm{SbCl_6}^-)_2$	379 (4.59), 530 (3.73)^b	
6a	457 (4.80)^a	516 (0.30)
6b	463 (4.82)^a	520 (0.25)
$\mathbf{7b}^{2+}(\mathrm{SbCl_6}^-)_2$	389 (4.80), 550 (3.85)^b	
11	275 (4.31)^a	
$\mathbf{12}^{2+}(\mathrm{BF_4}^-)_2$	390 (4.26), 543 (3.79)^b	

^{a} In $\mathrm{CH_2Cl_2}$. ^{b} In MeCN. ^{c} λ_{ex} 366 nm. The Φ_f values were determined using 9,10-diphenylanthracene as a standard.

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(7) **Crystal data for 6a**: $\mathrm{C_{50}H_{28}S_8}$, MW = 885.25, monoclinic $P2_1/c$, a = 18.408(7), b = 14.645(7), c = 30.55(1) Å, β = 102.50(3)°, V = 8039(6) Å^3, Z = 8, D_{calcd} = 1.463 g/cm^3, R_1 = 0.07, wR_2 = 0.146, S = 1.34. Structural disorder was observed for a terminal thiophene unit of molecule 2 by 180° rotation about the bithienyl axis, and the structural analysis could be converged by assuming the 20% contribution of minor conformer. **11**: $\mathrm{C_{34}H_{20}S_4}$, MW = 556.77, triclinic $P\bar{1}$, a = 14.798(5), b = 18.05(1), c = 20.15(1) Å, α = 79.85(5)°, β = 90.00(4)°, γ = 76.79(4)°, V = 5154(4) Å^3, Z = 8, D_{calcd} = 1.435 g/cm^3, R_1 = 0.072, wR_2 = 0.247, S = 3.44. **12**: $\mathrm{C_{34}H_{20}S_4}^{2+}(\mathrm{SbCl_6}^-)_2\cdot(\mathrm{C_2H_3N})_2$, MW = 1307.81, monoclinic $C2/c$, a = 15.867(7), b = 14.301(6), c = 21.379(8) Å, β = 92.66(3)°, V = 4846(3) Å^3, Z = 4, D_{calcd} = 1.792 g/cm^3, R_1 = 0.059, wR_2 = 0.208, S = 3.72.

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lengths can be rationalized by the conformational change as revealed by X-ray analysis that the planar conformation of the sexithiophene unit in **6a**,**b** changes to a twisted conformation in the dications **7a**,**b**$^{2+}$. The conformational change is considered to be brought about by Coulomb repulsion between the two thioxanthylium ions in the dications.

Drastic molecular structural change causes the hysteretic redox properties of the neutral oligothiophenes and dications. Oxidation peak of **6b** was observed at +0.67 V, which corresponds to the bond-breaking reaction of the hexaarylethane bond to give dication **7b**$^{2+}$. On the other hand, the corresponding reduction peak appeared in the far cathodic region (+0.35 V), which is assigned to the reduction peak of dication **7b**$^{2+}$ ascribing to the reduction of thioxanthylium parts. The hexaarylthane bond is regenerated in this process. Such redox behavior has been commonly observed in the similar redox couples undergoing reversible C−C bond breaking [**1**, $E_p^{ox} = +0.88$ V versus SCE in CH_2Cl_2; **4**, +0.78 V; **6a**, +0.67 V; **11**, +0.84 V]/making [**2**$^{2+}$, $E_p^{red} = +0.28$ V in MeCN; **5**$^{2+}$, +0.34 V; **7a**$^{2+}$, +0.36 V; **12**$^{2+}$, +0.39 V]. This result indicates that the present system has a high electrochemical bistability.[4] The oxidation potentials are shifted to negative potentials as the number of thiophene units increases. This is explained by considering that the electron-donating ability of thiophene oligomers increases with an increase of π-conjugation. On the other hand, the dication **7b**$^{2+}$ containing a sexithiophene with alkyl groups exhibited a reversible 2e oxidation peak owing to the oligothiophene at +1.09 V as shown in Figure 4b. In contrast to **7b**$^{2+}$, **7a**$^{2+}$ showed two cathodic return peaks corresponding to the oligothiophene part and a sharp reduction peak at +0.43 V due to the thioxanthylium part, which is almost reversible (Figure 4a). When the electrochemical oxidation and reduction are constantly repeated in **6a**, the peak currents increased, indicating the formation of an electrochemically active polymer. It is noteworthy that bithiophene derivative **1** and quaterthiophene derivative **4** did not show polymerization, thus indicating that lower oxidation potentials are necessary for the polymerization. The detailed study on this unique polymer containing poly-redox active sites is currently underway.

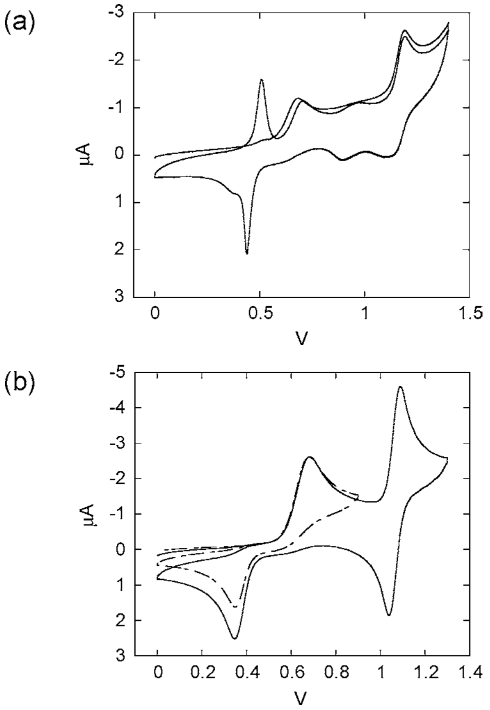

Figure 4. Cyclic voltammograms of (a) **6a** and (b) **6b** (hysteretic interconversion between **6b** and **7b**$^{2+}$ is shown as a dashed line).

In this paper, we have succeeded in preparing redox active oligothiophenes containing a redox active hexaarylethane unit, in which C−C bond making/breaking is reversibly induced upon electron transfer. This system shows a remarkable electrochemical bistability accompanied by hysteresis of redox potentials. The thiophene units could be easily modified, and a sexithiophene oligomer was prepared here. By using this unique thiophene oligomer, it would be possible to develop molecular wires with switching functions.

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Supporting Information Available: Detailed experimental procedures, X-ray analyses of compounds **6a**, **11**, and **12**$^{2+}$$(SbCl_6^-)_2$, and crystal data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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