

Synthesis and Properties of Novel Oligothiophenes Surrounded by Bicyclo[2.2.2]octene Frameworks

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Novel oligothiophenes surrounded by bicyclo[2.2.2]octene (abbreviated as BCO) frameworks ranging from dimer to hexamer, **1**(*n*T) (*n* = 2, 3, 4, 6), were prepared, and their structures and electronic properties were investigated. Dimer **1**(2T) was synthesized by oxidative coupling of the 2-lithiated monomer generated from 4,5-BCO-annulated 2-bromothiophene **8** with CuCl₂ in 76% yield. Trimer **1**(3T) and tetramer **1**(4T) were synthesized by Stille coupling of 2,5-dibromo-3,4-BCO-annulated thiophene **4** and of the 5,5'-dibromo derivative of bis(3,4-BCO-thiophen-2-yl) **10** with 2-stannylated 4,5-BCO-annulated thiophene **9** in 41% and 46% yield, respectively. Hexamer **1**(6T) was synthesized by oxidative coupling of terthiophene **12**, tris-annulated with BCO units, in 81% yield. X-ray crystallographic studies showed that the thiophene rings in **1**(2T) and **1**(3T) are rotated around the inter-ring C–C bond(s) with the C=C–C=C dihedral angles of –174.3(5)° for **1**(2T) and –149.7(3)° and 34.4(3)° for **1**(3T). In the crystal structures of **1**(2T) and **1**(3T), no π -stacking was observed as expected from the steric effect of the BCO units. Theoretical calculations for **1**(2T) and **1**(3T) at the B3LYP/6-31G(d) level indicated that the annulation with BCO units either at the 2,3- or 3,4-positions of thiophene rings raises both the KS HOMO and LUMO levels. In the electronic absorption spectra of **1**, the longest wavelength absorption band corresponding to the π – π^* transition is bathochromically shifted with the increase in absorption intensity as the number of thiophene rings increases, and the absorption of the polythiophene **1** with infinite length was predicted to be 419 nm. The cyclic voltammetry of **1** in CH₂Cl₂ at –78 °C (2T) or at room temperature (3T, 4T, 6T) showed two reversible oxidation waves, indicating that the radical cation and dication of **1** are stable under these conditions.

Introduction

There is growing interest in oligothiophenes^{1–3} as components of organic electronic devices such as thin film transistors, photovoltaic solar cells, and light-emitting diodes,² since oligothiophenes have more ordered molecular and crystalline structures than the corresponding polymers. Oligothiophenes are also expected to play an important role in molecular electronics,³ which are currently attracting considerable attention from the viewpoint of nanotechnology in a new generation. Furthermore, the study of oligothiophenes is important for elucidation of the conduction mechanism of polythiophenes and related polymers.¹ Polythiophenes are known to show high electric conductivity under p-doped conditions.^{1a} Thus, the radical cation and dication of oligothiophenes are considered as important models of partial structure(s) of p-doped polythiophene, i.e., polaron or bipolaron.⁴

On the other hand, there has been much discussion about the occurrence and nature of the intermolecular interaction, i.e., the formation of π -stacked⁵ or σ -bonded⁶ dimer of the radical cation (polaron) and about its relation to the dicationic state (bipolaron). Although it is quite important to elucidate the unimolecular electronic properties of cationic oligothiophenes for clarification of the conduction mechanism, it has been confronted with great difficulty due to this intermolecular interaction, and various efforts are being made to clarify the nature of the dicationic state on a single chain.^{7,8} In our previous works, we have shown that the structural modification of the cyclic π -conjugated systems by annulation with bicyclo[2.2.2]octene (abbreviated as BCO) frameworks is quite effective in stabilizing the π -systems,^{9,10} including

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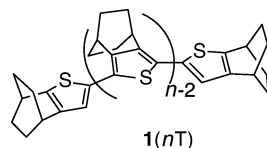
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sulfur-containing systems such as thiophenes¹¹ and dithiins,^{12,13} when they are positively charged. For these BCO-modified π -conjugated systems, the prevention of intermolecular π -electronic interactions has been demonstrated in the solid-state structures.^{10e,11,12} So we decided to synthesize a series of oligothiophenes totally surrounded by BCO frameworks, **1**(*n*T).



In compounds **1**(*n*T), the reactive two ends of the oligomeric chain are capped with BCO units, and in the middle part of the molecule, the 3,4-positions of thiophene units are also fused with BCO units, which is expected to prevent the formation of either the π - or σ -dimer after one- or two-electron oxidation. This latter structural feature is expected to have particular significance for the elucidation of unimolecular properties of the cationic oligothiophene. In the present paper, we report the synthesis of a series of novel oligothiophenes **1**(*n*T) (*n* = 2, 3, 4, 6) and their structural, spectroscopic, and electrochemical properties together with some discussion on the theoretical evaluation of the effect of annelation with BCO units on the electronic properties of thiophene rings.

Results and Discussion

Synthesis. First we describe the preparative method of each of the thiophene units that are structurally modified by the BCO frameworks. By the appropriate cross (or homo) coupling of these thiophene units, a series of oligothiophenes **1**(*n*T) can be prepared.

For the synthesis of 3,4-bicyclo[2.2.2]octanothiophene, that is, the central thiophene unit in oligomer **1**, we made use of the Hinsberg method.¹⁴ As shown in Scheme 1, the condensation of bicyclo[2.2.2]octane-2,3-dione (**2**)¹⁵ with dimethyl thiodiacetate in the presence of *t*-BuOK followed by hydrolysis of the produced diester gave 3,4-bicyclo[2.2.2]octanothiophene-2,5-dicarboxylic acid (**3**), which was then bromodecarboxylated¹⁶ to afford dibromide **4** in 42% yield.

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On the other hand, for the synthesis of 2,3-bicyclo[2.2.2]octenothiophene to be used as a terminal block in **1**, a method reported by Hauptmann et al.¹⁷ was employed in the second step. Thus, lithiation of 2,3-dibromobicyclo[2.2.2]oct-2-ene (**5**) with 2 equiv of *tert*-butyllithium in THF at $-100\text{ }^{\circ}\text{C}$ followed by addition of DMF gave 2-bromo-3-formylbicyclo[2.2.2]oct-2-ene (**6**) in 86% yield. Treatment of **6** with ethyl mercaptoacetate in an ethanolic solution of sodium alkoxide gave thiophenecarboxylate ester **7** in 77% yield, which was hydrolyzed and bromodecarboxylated to give **8** in 34% yield.

Then, as shown in Scheme 2, dimer **1**(2T) was synthesized as pale yellow crystals by oxidative coupling, using CuCl_2 as an oxidant, of the lithiated thiophene generated from **8**, in 76% yield. Trimer **1**(3T) and tetramer **1**(4T) were synthesized by Stille coupling of monobromide **8** and dibromide **10** with 2-stannylatedthiophene **9**, which had been prepared from **8** by lithiation and stannylation: dibromide **10** had been prepared by oxidative coupling of monolithiated bromide obtained from dibromide **4**. For the synthesis of hexamer **1**(6T), the oxidative dimerization of terthiophene **12**, which can be obtained by Stille coupling of bromobithiophene **11** with **9**, was conducted using 2 equiv of $\text{NO}^+\text{SbF}_6^-$ in CH_2Cl_2 : **1**(6T) was obtained in 81% yield as a yellow solid.

Structures of 1(2T) and 1(3T). The molecular structure of dimer **1**(2T) was determined by X-ray crystallography at $-173\text{ }^{\circ}\text{C}$. The crystal structure involved the statistical disorder in the thiophene rings arising from a 180° rotation around the inter-ring C–C bond. Such a type of rotational disorder has also been observed in unsubstituted bithiophene.¹⁸ In the present case, the occupancy ratios of four disordered points for sulfur atoms were almost identical, and hence, the conformation of **1**(2T) in the solid state could not be determined only from the diffraction data. However, since recent high-level theoretical calculations for unsubstituted bithiophene indicated that the transoid-conformation is more stable than the cisoid-conformation,¹⁹ we refined the diffraction data as transoid-structures, as shown in Figure 1. The torsion angle (C3–C4–C5–C6) between the two thiophene rings was $-174.3(5)^{\circ}$, which was smaller than the calculated value (-158.2°) obtained by the DFT calculations for dimer **1**(2T) at the B3LYP/6-31G(d) level. The observed smaller twisting is most probably ascribed to the effect of packing force. The similar results have also been observed for unsubstituted bithiophene (**13**); the thiophene rings are planarized (twisted angle, 180°) in the solid state¹⁸ while twisted in the gas phase with a dihedral angle of 146° .²⁰ The B3LYP calculations gave a value of 158.2° (B3LYP/6-31G(d)).

The observed bond lengths (\AA) in the thiophene rings [S1–C1, 1.721(2); C1–C2, 1.353(3); C2–C3, 1.423(6); C3–C4, 1.318(6); C4–S1, 1.785(2); C4–C5, 1.455(3)]

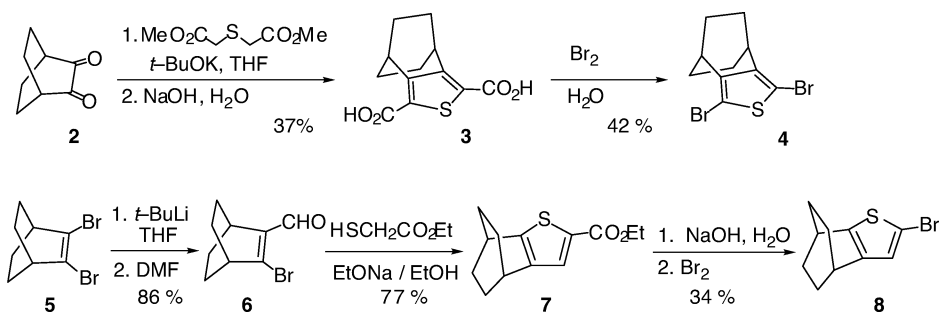
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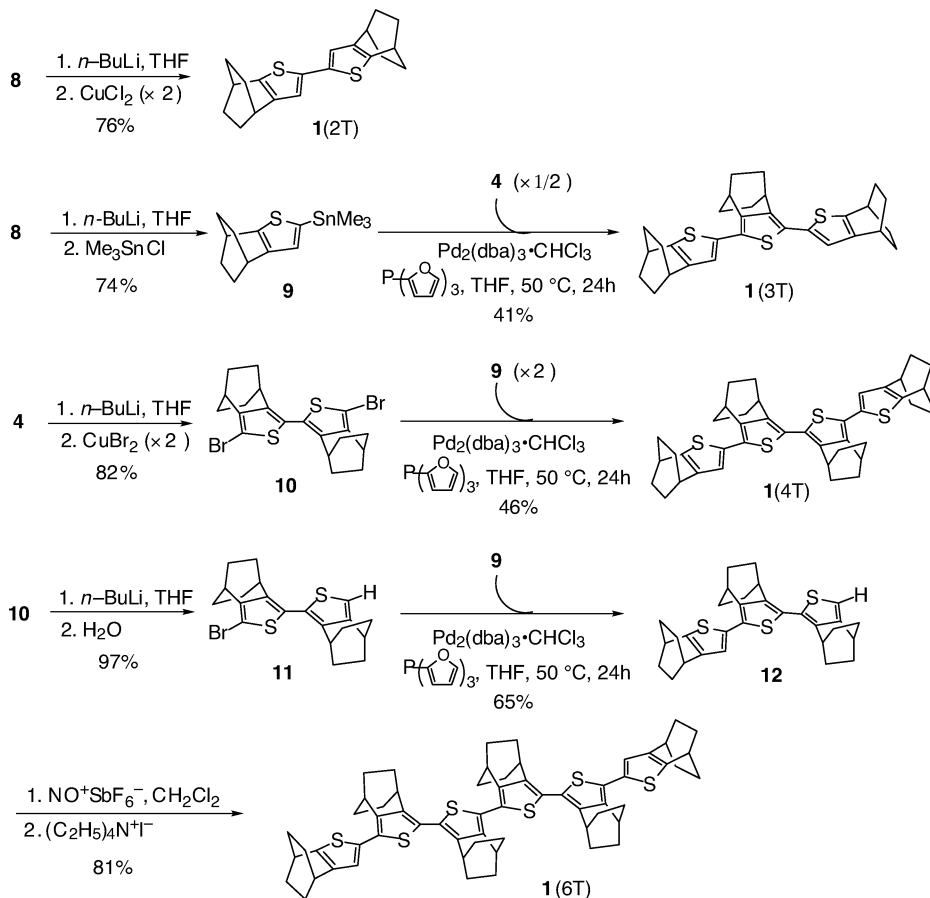
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SCHEME 1



SCHEME 2



shown in Figure 1a are in fairly good agreement with those of the structure optimized at the B3LYP/6-31G(d) level (S1–C1, 1.735; C1–C2, 1.371; C2–C3, 1.422; C3–C4, 1.381; C4–S1, 1.767; C4–C5, 1.449) and also with those reported for unsubstituted bithiophene [S1–C1, 1.694(2); C1–C2, 1.354(3); C2–C3, 1.444(3); C3–C4, 1.425(3); C4–S1, 1.720(2); C4–C5, 1.444(3)],¹⁸ indicating that the annelation with BCO units imposes almost no steric strain upon the intrinsic geometry of bithiophene itself.

In the crystal packing structure of **1(2T)** shown in Figure 1b, two toluene molecules are included in a unit cell and the bithiophene rings are arranged in a considerably slipped face-to-face fashion. The shortest intermolecular distance between the sp²-carbons is quite large (5.051 Å) due to the steric effect of the bicyclic σ -frameworks, and apparently no π -stacking interaction is present in the solid state.

The molecular structure of trimer **1(3T)** was also determined by X-ray crystallography at $-150\text{ }^{\circ}\text{C}$ (Figure 2). In this case, similar statistical disorder in the terminal thiophene rings was also observed, and the dominant type was resolved as a cisoid-transoid conformation with the torsion angles of C3–C4–C5–C6 and C7–C8–C9–C10 being $-149.7(3)^{\circ}$ and $34.4(3)^{\circ}$, respectively. For comparison, theoretical calculations (B3LYP/6-31G(d)) were performed again for **1(3T)** with symmetric constraint for the all-transoid conformer (C_3) and for the all-cisoid conformer (C_3). On the basis of Hartree–Fock energy, the all-transoid conformer was shown to be slightly more stable than the all-cisoid conformer by 0.57 kcal mol⁻¹. As for the torsion angles between the thiophene rings, -149.5° was obtained for the all-transoid conformer and 40.4° for the all-cisoid conformer, in good agreement with the observed values. According to theoretical calculations for parent terthiophene (**14**), the

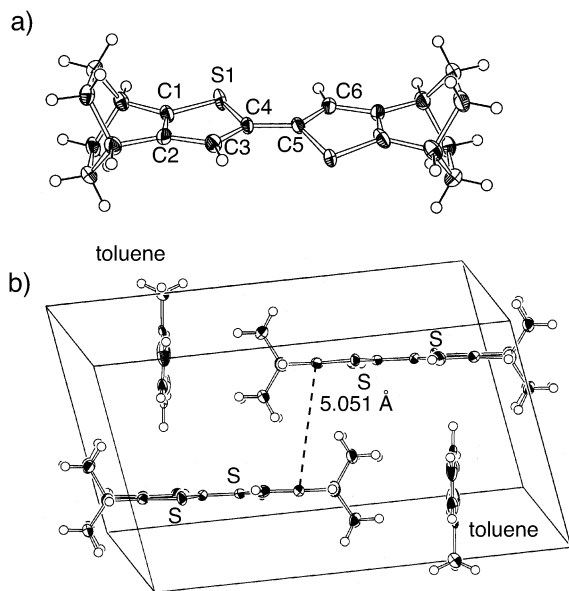


FIGURE 1. (a) ORTEP drawing of dimer **1(2T)**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg) are S1–C1, 1.721(2); C1–C2, 1.353(3); C2–C3, 1.423(6); C3–C4, 1.318(6); C4–S1, 1.785(2); C4–C5, 1.455(3); C1–S1–C4, 87.3(1); S1–C1–C2, 119.6(2); C1–C2–C3, 103.5(3); C2–C3–C4, 120.8(4); C3–C4–S1, 108.8(3); C3–C4–C5–C6, 174.3(5). (b) Crystal packing drawings showing the X-ray crystal structure of **1(2T)**, including the shortest intermolecular distance of C(sp²)–C(sp²).

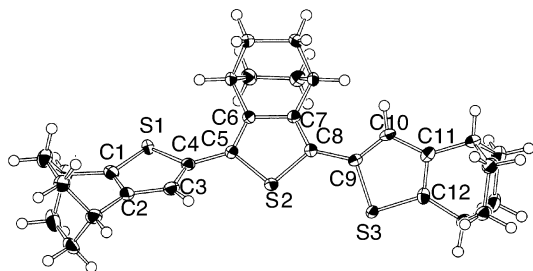


FIGURE 2. ORTEP drawing of trimer **1(3T)**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg) are S1–C1, 1.701(2); C1–C2, 1.355(2); C2–C3, 1.425(4); C3–C4, 1.351(4); C4–S1, 1.751(2); C4–C5, 1.452(2); C5–C6, 1.371(2); C6–C7, 1.424(2); C7–C8, 1.363(2); S2–C5, 1.742(2); S2–C8, 1.740(2); C8–C9, 1.465(2); C9–C10, 1.338(4); C10–C11, 1.423(4); C11–C12, 1.352(2); S3–C9, 1.749(2); S3–C12, 1.726(2); C1–S1–C4, 90.53(9); S1–C1–C2, 115.0(1); C1–C2–C3, 109.0(2); C2–C3–C4, 115.6(3); C3–C4–S1, 109.7(2); S2–C5–C6, 110.00(1); C5–C6–C7, 113.3(1); C6–C7–C8, 114.0(1); C7–C8–S2, 109.9(1); C8–S2–C5, 92.8(1); S3–C9–C10, 110.9(2); C9–C10–C11, 115.2(7); C10–C11–C12, 109.9(2); C11–C12–S3, 114.1(1); C12–S3–C9, 89.9(1); C3–C4–C5–C6, –149.7(3); C7–C8–C9–C10, 34.4(3).

inter-ring rotation for an all-anti conformer (162.2°) was found to be smaller than that of **1(3T)**, suggesting that there is some steric repulsion between the bridgehead hydrogen of the BCO unit in the central building block and sulfur atom of the adjacent thiophene ring. On the other hand, the bond lengths and angles of the central thiophene ring were comparable to those of terminal thiophene rings and also to those reported for alkyl-substituted terthiophenes.²¹ This indicates again that the annelation with BCO units at the 3,4-positions imposes

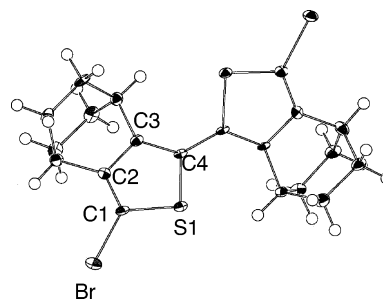


FIGURE 3. ORTEP drawing of **10**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg) are S1–C1, 1.744(6); C1–C2, 1.346(9); C2–C3, 1.423(8); C3–C4, 1.389(8); C4–S1, 1.744(6); C1–S1–C4, 91.6(3); S1–C1–C2, 112.0(5); C2–C3–C4, 113.4(5); C3–C4–S1, 110.4(4).

almost no steric strain upon the thiophene ring itself, just like the case of annelation at the 2,3-positions. In the crystal packing structure of **1(3T)**, no π -stacking was observed, as in the case of **1(2T)**.

The structure of a dibromide of 3,4-BCO-annelated bithiophene **10** was also determined by X-ray crystallography (Figure 3). In this case, the only transoid-conformer was refined without disorder. Apparently, great steric repulsion between the two BCO units would be present in a cisoid-conformer. In the X-ray structure, some rotation between the two thiophene rings [–141.0(7)°] was observed, which was quite similar to the case of **1(3T)**, due to the same steric reason as described above.

Electronic Properties. To examine the effects of BCO-annelation upon the electronic state of each single component of the oligothiophenes, theoretical calculations (B3LYP/6-31G(d)) were carried out for parent thiophene (**15**), 3,4-bicyclo[2.2.2]octanothiophene (**16**), and 2,3-bicyclo[2.2.2]octenothiophene (**17**) to give the results shown in Figure 4. Thus, the Kohn–Sham (KS) HOMO levels of **16** and **17** are elevated by 0.33 and 0.58 eV, respectively, with reference to that of parent compound **15**, apparently due to the inductive and hyperconjugative effects of annelated BCO frameworks. The observed greater elevation of the HOMO level in **17** can be rationalized by the fact that the KS HOMO of thiophene lies on the butadiene moiety and its coefficient at the 2,5-positions is larger than that at the 3,4-positions. Since the extent of elevation of the KS LUMOs of **16** and **17** are smaller and quite similar for **16** and **17** (0.23 and 0.25 eV, respectively), the HOMO–LUMO energy gap is smaller for **17**.

Next, the HOMO–LUMO levels of **1(2T)** and **1(3T)** were compared with those of parent bithiophene **13** and terthiophene **14**. As shown in Figure 5, the HOMO levels in **1(2T)** and **1(3T)** are elevated by 0.62 and 0.45 eV, respectively, compared with those of the corresponding parent compounds **13** and **14**, similarly to the case of the component units **16** and **17**, as described above. The LUMO levels in **1(2T)** and **1(3T)** are also elevated compared with **13** and **14**. In the case of **1(2T)**, the extent of elevation of HOMO is larger than that of LUMO, which

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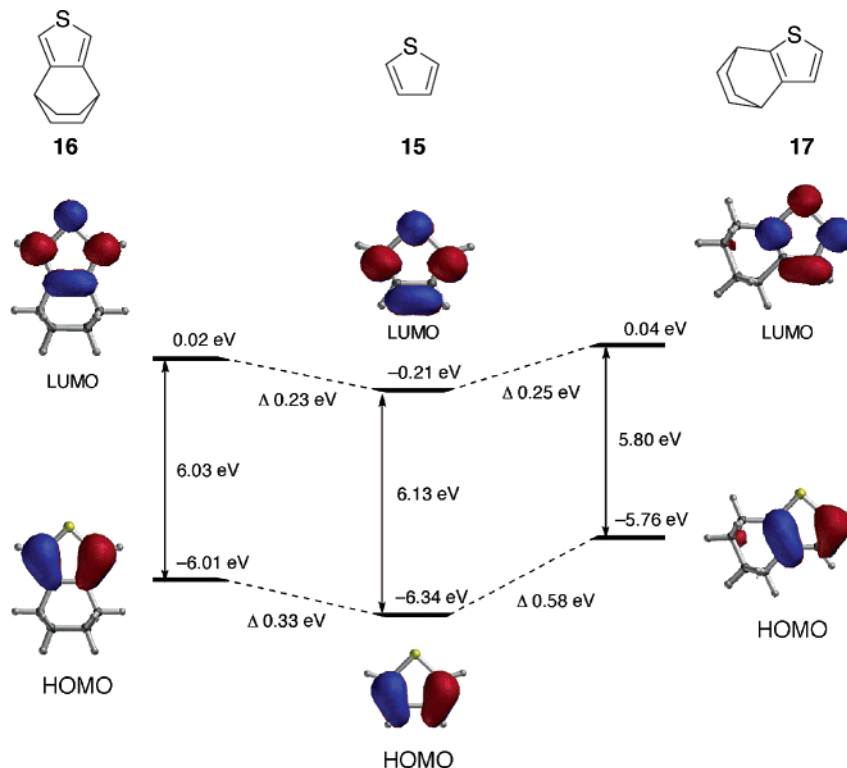


FIGURE 4. The KS HOMO and LUMO orbitals and their energies calculated at the B3LYP/6-31G(d) level of theory for thiophenes 15–17.

TABLE 1. Longest Wavelength Absorption Bands for Oligothiophenes **1** and **18** [λ_{\max} (log ϵ)]^a

	2T	3T	4T	6T
1	332 (4.19)	363 (4.36)	372 (4.37)	383 (4.54)
18 ^b	329 (4.16)	376 (4.43)	408 (4.56)	431 (4.44)

^a In CH₂Cl₂. ^b Reference 22.

leads to a decrease in the HOMO–LUMO energy gap by BCO annelation. In the case of **1**(3T), however, the extent of elevation of HOMO is much smaller than that in **1**(2T), resulting in an increase in the HOMO–LUMO energy gap. This decrease in the extent of elevation of HOMO in **1**(3T) could be ascribed to the distortion of the conjugated π -system: the terthiophene system in **1**(3T) has a more twisted conformation (C3–C4–C5–C6; -149.5°) than that of the mother compound **14** (C3–C4–C5–C6: -162.2°) due to the repulsion between bridge-head hydrogens of the BCO group in the central unit and sulfur atoms of the adjacent thiophene.

Electronic Absorption Spectra of Oligothiophenes

1. The electronic absorption spectra of a series of BCO-annelated oligothiophenes **1** in CH₂Cl₂ are shown in Figure 6. The longest wavelength absorption of **1**, which is reasonably ascribed to the HOMO→LUMO (π – π^*) transition, is bathochromically shifted with a concomitant increase in absorption intensity, in accord with the extension of the π -systems. Compared with a series of oligothiophenes end-capped with cyclohexene **18**, the longest wavelength absorption band of **1**(2T) is observed

at a slightly longer wavelength than the corresponding **18**(2T),²² but for the longer oligothiophenes **1**(3T, 4T, 6T), the absorption was found to be in the shorter wavelength region (Table 1). This apparently reflects the presence of larger torsion angle(s) between the thiophene rings for BCO-annelated oligothiophenes than those without any substituents, due to the steric reasons as has been described.

In a series of oligothiophenes, (thiophene)_n, a linear relationship has been theoretically²³ predicted and experimentally shown²⁴ between the π – π^* -transition energy and the inverse chain length ($1/n$). This correlation appears to be present for a series of BCO-annelated oligothiophenes in the present work, as shown in the inset of Figure 6. Although the linearity is not so good, from the extrapolation of the data for **1**, the longest wavelength absorption for the fully BCO-annelated polythiophene consisting of a regular infinite chain is predicted to appear approximately at $\lambda_{\max} = 419$ nm (2.96 eV).

Electrochemistry. To examine the redox behavior of newly synthesized oligothiophenes **1**, cyclic voltammetry was conducted in CH₂Cl₂ at room temperature or at -78°C . The voltammograms are shown in Figure 7 and the values of oxidation potentials are summarized in Table 2 together with those for oligothiophenes end-capped with

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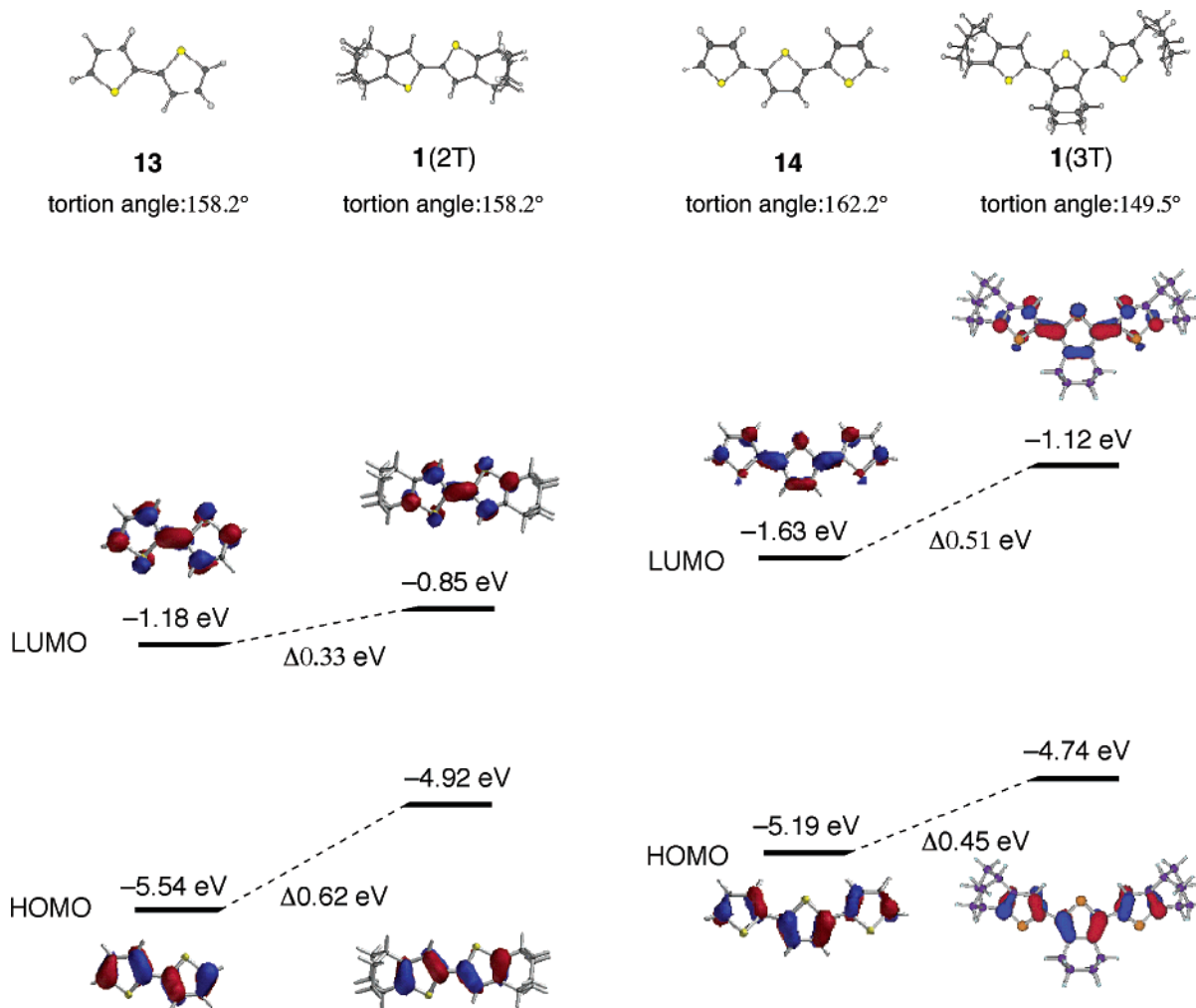


FIGURE 5. The KS HOMO and LUMO orbitals and their energies calculated at the B3LYP/6-31G(d) level of theory for bithiophenes **13** and **1(2T)** and for terthiophenes **14** and **1(3T)**. The torsion angles in their optimized structures are included.

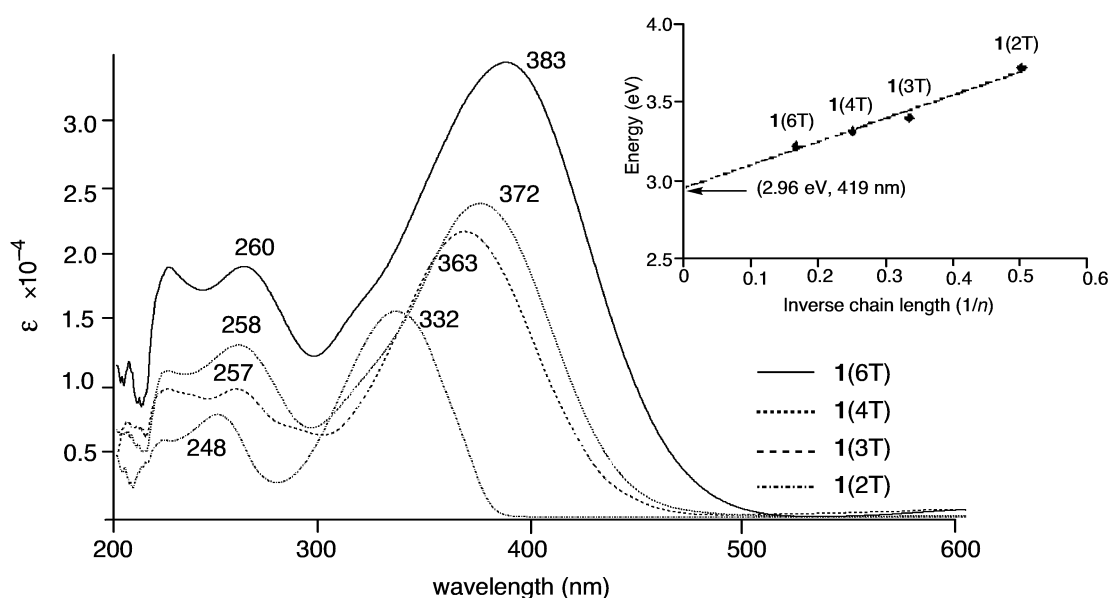


FIGURE 6. Electronic absorption spectra of oligothiophenes **1(nT)** in CH_2Cl_2 and its correlation (inset) of the longest wavelength absorption with the inverse chain length ($1/n$).

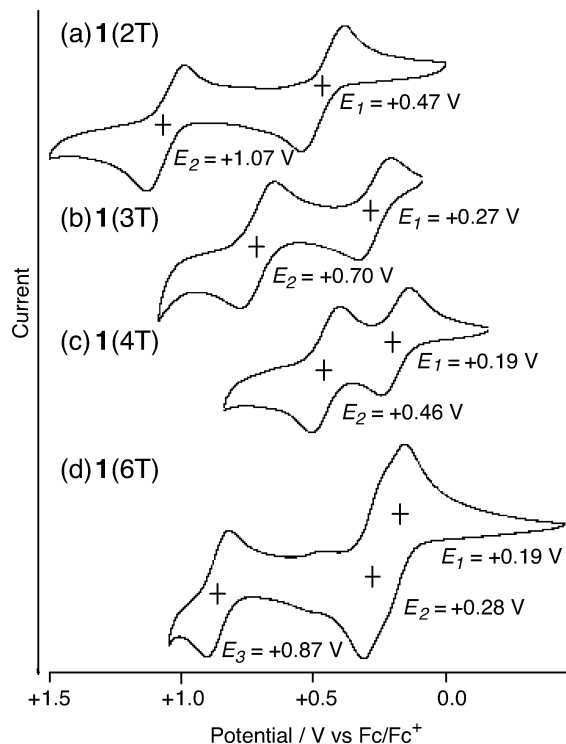


FIGURE 7. Cyclic voltammograms of **1** in CH_2Cl_2 containing $\text{Bu}_4\text{N}^+\text{PF}_6^-$ (0.1 M) with a scan rate of 100 mV s^{-1} : (a) **1**(2T) at -78°C under vacuum, (b) trimer **1**(3T) at room temperature under vacuum, (c) tetramer **1**(4T) at room temperature, and (d) hexamer **1**(6T) at -78°C under argon.

TABLE 2. Redox Potentials^a of Oligothiophenes **1** and **18**^b

	1		18	
	E_1 (V)	E_2 (V)	E_1 (V)	E_2 (V)
2T	+0.47	+1.07	(+0.53) ^c	(+1.20) ^c
3T	+0.27	+0.70	+0.38	(+0.79) ^c
4T	+0.19	+0.46	+0.32	+0.66
6T	+0.19	+0.28	+0.22	+0.41

^a Potentials vs Fc/Fc^+ . ^b Reference 24. ^c Irreversible wave.

cyclohexene **18**²⁵ for comparison. All the oligothiophenes **1** exhibited reversible first oxidation waves at room temperature. The reversibility of **1**(2T) clearly indicated the enhanced stability of the corresponding radical cations as compared with that of **18**(2T), which showed only an irreversible first oxidation wave. Furthermore, the annelation with BCO units both at the middle and at the ends of the oligothiophene chains is shown to lower both the first and second oxidation potentials as compared with **18**. As concerns the second oxidation waves, **1**(3T), **1**(4T), and **1**(6T) showed well-defined reversible waves at room temperature, while **1**(2T) exhibited a reversible wave with $E_{1/2} = +1.07 \text{ V}$ only at -78°C under vacuum. Thus, under the appropriate conditions, dications of oligothiophenes **1** are shown to be also stable. In the case of hexamer **1**(6T), a reversible third oxidation wave was also observed at $E_{1/2} = +0.87 \text{ V}$, suggesting the possibility of the generation of a radical trication of **1**(6T) as a stable species.

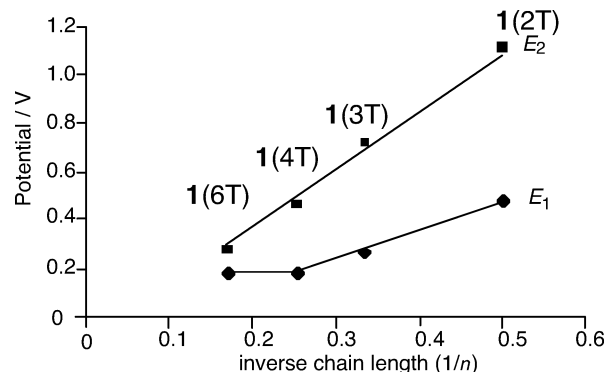


FIGURE 8. Correlation of the first and second oxidation potentials of the oligothiophenes **1**($n\text{T}$) with the inverse chain length ($1/n$).

In a manner similar to the electronic absorption spectra, the correlations of first and second oxidation potentials of oligothiophenes **1** with the inverse chain length^{22,26} were examined, and the results are shown in Figure 8. As described above, the oxidation potential of **1** was gradually lowered with the increasing size of the π -system. However, a saturation phenomenon was observed for the first oxidation potential as the size of oligothiophene reached tetramer **1**(4T): no further lowering of the oxidation potential was observed as the size increased and reached hexamer **1**(6T). In contrast, the relationship was linear for the second oxidation potential in the range of **1**(2T) to **1**(6T), so that the difference in oxidation potential [$\Delta(E_1 - E_2)$] becomes quite small in the case of **1**(6T).

These observations clearly reflect the interplay of two major effects of the annelation with BCO frameworks. First, the steric repulsion between the bridgehead hydrogen of the BCO unit, in the middle part of **1**, and sulfur atoms in the adjacent thiophene rings causes some rotation around the inter-ring bonds and the distortion of the π -system, which is not favorable for effective π -conjugation. Despite such unfavorable distortion of the π -system from planarity, the electron donation of the BCO systems by σ - π -conjugation and inductive effects do operate so that the oxidation potentials are lowered and the produced cationic species (radical cations and dications) are expected to be stabilized considerably.

Conclusion

In summary, we have shown the synthesis of novel oligothiophenes **1**($n\text{T}$) ($n = 2, 3, 4, 6$) surrounded by rigid bicyclic σ -frameworks, i.e., bicyclo[2.2.2]octane (BCO) units. On the basis of the results of X-ray structural analysis, theoretical calculations, and also the comparison of the longest wavelength absorption with those of end-capped oligothiophenes **18**, the central thiophene rings of **1** were shown to be more distorted than **18** in their neutral states. However, judging from the lower oxidation potentials than those of **18**, the distortion of the π -system is considered not to affect the stability of the cationic species formed by one- or two-electron

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oxidation. Thus, oligothiophenes **1** are considered to be the appropriate system for the study on the unimolecular electronic properties of cationic oligothiophenes, and efforts are now being made to clarify the properties of radical cations and dications of these oligothiophenes, the results of which will be reported in the near future.

Experimental Section

General Procedures. Chemical shifts of ^1H (300 MHz) and ^{13}C (75.4 MHz) NMR spectra are reported in ppm with reference to tetramethylsilane, using the signal of solvents as internal standard (δ 7.26, 5.32, or 7.15 for CHCl_3 , CH_2Cl_2 , or C_6H_6 in ^1H NMR and δ 77.0, 54.0, 128.4 in ^{13}C NMR for CDCl_3 , CD_2Cl_2 , or C_6D_6 , respectively). Preparative gel-permeation chromatography (GPC) was performed with a JAI LC-908 chromatograph equipped with JAIGEL 1H and 2H columns.

All reactions were carried out under an argon atmosphere unless otherwise noted. THF, ether, and toluene were distilled from sodium benzophenone ketyl. Dichloromethane, hexane, and DMF were distilled over CaH_2 . Ethanol was distilled over K_2CO_3 . $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ was synthesized according to the literature procedure.²⁷ All commercially available materials were of reagent grade unless otherwise noted.

Computational Method. All calculations were conducted using Gaussian 98 programs.²⁸ The geometries were optimized with the restricted Becke hybrid (B3LYP) at 6-31G(d) level. The optimization was carried out based on appropriate symmetries, i.e., C_2 and C_s for **1**(3T) and **14**, respectively.

2,5-Dibromo-3,4-bicyclo[2.2.2]octanethiophene (4). A solution of *t*-BuOK (1.34 g, 11.9 mmol) in THF (20 mL) was added to a stirred solution of dimethyl thiodiacetate²⁹ (0.968 g, 5.43 mmol) and bicyclo[2.2.2]octane-2,3-dione (**2**)¹⁵ (0.500 g, 3.62 mmol) in THF (10 mL) via a cannula. The mixture was stirred and heated at 45 °C for 5 h. After cooling the mixture, 100 mL of water was added, and THF was removed by evaporation under reduced pressure. To the aqueous solution of the crude mixture was added 50 mL of 4 N aqueous solution of NaOH, and the solution was refluxed for 12 h. After being allowed to cool to room temperature, the solution of produced **3** was neutralized with 10% HCl, and a solution of bromine (1.20 g, 7.51 mmol) in 10 mL of hexane was added dropwise to the solution at 70 °C over 1 h with continuous stirring. During the addition of bromine, an adequate amount of 1 N NaOH was occasionally added to maintain the pH of the solution in the range of 7.0 ± 1.0 . Then the reaction mixture was extracted with ether, and the ethereal solution was dried over MgSO_4 . The volatiles were removed in vacuo, and the crude product was purified by flash chromatography over SiO_2 with CH_2Cl_2 as an eluent to give **4** (0.486 g, 41.7% based on **2**) as a colorless solid: mp 83.6–84.7 °C; ^1H NMR (CDCl_3) δ 3.09 (m, 2H), 1.57 (m, 4H), 1.42 (m, 4H); ^{13}C NMR (CDCl_3) δ 144.6, 100.8, 30.3, 25.4; EI MS m/z 322 (M^+); HRMS calcd for $\text{C}_{10}\text{H}_{10}\text{Br}_2\text{S}$: 319.8870, found 319.8859. Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{Br}_2\text{S}$: C, 37.29; H, 3.13. Found: C, 36.99; H, 3.13.

2-Bromo-3-formylbicyclo[2.2.2]oct-2-ene (6). A solution of *tert*-butyllithium in pentane (1.51 M, 2.60 mL, 3.93 mmol)

was added to a stirred solution of 2,3-dibromobicyclo[2.2.2]oct-2-ene (**5**)^{10b} (0.499 g, 1.88 mmol) in THF (20 mL) at –110 °C within 15 s. After 4 min, DMF (700 μL , 0.661 g, 9.04 mmol) was added and then the cooling bath was removed to let the mixture warm to room temperature. The reaction mixture was quenched with 10% aqueous solution of HCl (30 mL) and extracted with ether, and the ethereal solution was dried over MgSO_4 . After the solution was evaporated under reduced pressure to give crude **6** (0.347 g, 86.0%) as a colorless oil, a part of **6** was purified by column chromatography (SiO_2 /hexane: CH_2Cl_2 = 1:1) for elemental analysis: ^1H NMR (CDCl_3) δ 9.76 (s, 1H), 3.38 (m, 1H), 2.98 (m, 1H), 1.60 (m, 4H), 1.29 (m, 4H); ^{13}C NMR (CDCl_3) δ 188.1, 144.4, 142.2, 44.5, 29.7, 26.0, 25.3; EI MS m/z 214 (M^+); HRMS calcd for $\text{C}_9\text{H}_{11}\text{BrO}$: 213.9993, found 213.9994. Anal. Calcd for $\text{C}_9\text{H}_{11}\text{BrO}$: C, 50.26; H, 5.15. Found: C, 50.08; H, 5.08.

2-Bromo-4,5-bicyclo[2.2.2]octenothiophene (8). A solution of **6** (0.409 g, 1.90 mmol) and ethyl mercaptoacetate (230 μL , 0.252 g, 2.10 mmol) in absolute ethanol (10 mL) was slowly added to a stirred solution of EtONa in EtOH, prepared from sodium (0.350 mg, 8.75 mmol) and absolute ethanol (14 mL). After being stirred at room temperature for 12 h, the reaction mixture was poured into ice–water and then neutralized with 10% HCl. The mixture was extracted with ether, dried over MgSO_4 , and evaporated under reduced pressure to give thiophenecarboxylate ester **7** (0.343 g, 76.3%) as a yellow oil: ^1H NMR (CDCl_3) δ 7.60 (s, 1H), 4.31 (m, 2H), 3.29 (m, 1H), 3.20 (m, 1H), 1.79 (m, 4H), 1.36 (m, 4H), 1.23 (m, 3H); ^{13}C NMR (CDCl_3) δ 163.0, 149.3, 144.5, 129.7, 128.2, 60.5, 31.5, 30.9, 26.7, 26.4, 14.2; EI MS m/z 236 (M^+). A solution of **7** (4.04 g, 17.1 mmol) and NaOH (5.00 g, 125 mmol) in 100 mL of water was heated to reflux for 12 h. After being cooled to room temperature, the resultant solution was neutralized with 10% H_2SO_4 . To this mixture was added a solution of bromine (4.00 g, 25.0 mmol) in 10 mL of hexane dropwise with heating at 70 °C over 1 h with continuous stirring. During the addition of bromine, an adequate amount of 1 N NaOH was occasionally added to maintain the pH of the solution in the range of 7.0 ± 1.0 , and an organic layer slowly separated out. The reaction mixture was then cooled, extracted with ether, dried over MgSO_4 , and evaporated in vacuo. The crude product was purified by flash chromatography ($\text{SiO}_2/\text{CH}_2\text{Cl}_2$) to give **8** (1.41 g, 33.9%) as a colorless oil: ^1H NMR (CDCl_3) δ 6.87 (s, 1H), 3.21 (m, 1H), 3.15 (m, 1H), 1.73 (m, 4H), 1.35 (m, 4H); ^{13}C NMR (CDCl_3) δ 144.2, 141.3, 126.8, 106.6, 31.2, 31.1, 27.2, 26.9; EI MS m/z 244 (M^+); HRMS calcd for $\text{C}_{10}\text{H}_{11}\text{BrS}$: 241.9764, found 241.9765.

Bithiophene 1(2T). A solution of *n*-butyllithium in hexane (1.60 M, 0.620 mL, 0.990 mmol) was added dropwise to a stirred solution of 2-bromothiophene **8** (0.241 g, 0.990 mmol) in THF (20 mL) at –78 °C. After stirring at –78 °C for 30 min, CuCl_2 (0.270 g, 2.01 mmol) was added in one portion, and the reaction mixture was gradually warmed to room temperature over a period of 1 h and stirred at room temperature for additional 12 h. The mixture was extracted with ether, the ethereal solution was dried over MgSO_4 , and the volatiles were removed in vacuo. The residue was subjected to preparative GPC eluted with CHCl_3 to afford bithiophene **1(2T)** (0.122 g, 75.5%) as a colorless solid: mp 217.8–219.1 °C; UV–vis (CH_2Cl_2) λ_{max} 223 nm (log ϵ 3.76), 248 (3.89), 332 (4.19); ^1H NMR (CDCl_3) δ 6.91 (s, 2H), 3.23 (m, 2H), 3.16 (m, 2H), 1.75 (m, 8H), 1.38 (m, 8H); ^{13}C NMR (CDCl_3) δ 144.6, 138.7, 133.3, 120.1, 31.3, 31.2, 27.4, 26.9; EI MS m/z 326 (M^+); HRMS calcd for $\text{C}_{20}\text{H}_{22}\text{S}_2$: 326.1163; found, 326.1176. Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{S}_2$: C, 73.57; H, 6.79. Found: C, 73.33; H, 6.79.

2-(Trimethylstannyl)-4,5-bicyclo[2.2.2]octenothiophene (9). A solution of *n*-butyllithium in hexane (1.50 M, 1.00 mL, 1.50 mmol) was added dropwise to a stirred solution of 2-bromothiophene **8** (0.367 g, 1.51 mmol) in THF (20 mL) at –78 °C. After stirring at –78 °C for 30 min, trimethyltin chloride (1.0 M in THF, 3.00 mL, 3.00 mmol) was added, and the reaction mixture was gradually warmed to room temper-

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ature over a period of 1 h and stirred at room temperature for additional 12 h. The crude mixture was washed with an aqueous solution of NH_4Cl , the aqueous layer was extracted with ether, and the ethereal solution dried over MgSO_4 . The volatiles were removed in vacuo, and the residue was purified by preparative GPC eluted with CHCl_3 to afford **9** (0.363 g, 73.5%) as a colorless solid: mp 105.2–107.3 °C; ^1H NMR (CDCl_3) δ 7.02 (t, 1H), 3.40 (m, 1H), 3.29 (m, 1H), 1.78 (m, 4H), 1.36 (m, 4H), 0.38 (m, 9H); ^{13}C NMR (CDCl_3) δ 146.0, 145.4, 131.8, 130.5, 31.8, 31.4, 27.4, 27.1, –8.10; EI MS m/z 326 (M^+); HRMS calcd for $\text{C}_{13}\text{H}_{20}\text{Sn}$, 326.0308; found, 326.0304.

Terthiophene 1(3T). A solution of 2,5-dibromothiophene **4** (0.234 g, 0.727 mmol), 2-stannylthiophene **9** (0.476 g, 1.45 mmol), $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (0.0752 g, 0.0727 mmol), and tri(2-furyl)phosphine (0.135 g, 0.582 mmol) in 80 mL of dry THF was stirred with heating at 50 °C for 2 days. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl , extracted with ether, and dried over MgSO_4 . The volatiles were removed in vacuo, and the residue was purified by preparative GPC eluted with CHCl_3 to afford **1(3T)** (0.144 g, 40.6%) as a yellow solid: mp 316.2–317.0 °C; UV–vis (CH_2Cl_2) λ_{max} 225 nm ($\log \epsilon$ 3.99), 257 (3.98), 363 (4.36); ^1H NMR (C_6D_6) δ 7.12 (s, 2H), 3.65 (m, 2H), 2.98 (m, 2H), 2.95 (m, 2H), 1.54 (m, 4H), 1.47 (m, 12H), 1.26 (m, 8H); ^{13}C NMR (C_6D_6) δ 145.1, 142.5, 140.5, 132.2, 126.3, 123.0, 31.9, 31.3, 28.0, 27.6, 26.7; EI MS m/z 488 (M^+); HRMS calcd for $\text{C}_{30}\text{H}_{32}\text{S}_3$, 488.1666, found 488.1685. Anal. Calcd for $\text{C}_{30}\text{H}_{32}\text{S}_3$: C, 73.72; H, 6.60. Found: C, 73.52; H, 6.52.

5,5'-Dibromo-3,4,3',4'-bis(bicyclo[2.2.2]octano)-2,2'-bithiophene (10). A solution of *n*-butyllithium in hexane (1.60 M, 1.94 mL, 3.10 mmol) was added dropwise to a stirred solution of 2,5-dibromothiophene **4** (0.999 g, 3.10 mmol) in THF (40 mL) at –78 °C over 2 min. After stirring for 30 min, CuBr_2 (1.40 g, 6.26 mmol) was added in one portion, and the reaction mixture was stirred at –78 °C for 30 min, and gradually warmed to room temperature over a period of 1 h. After additional stirring for 12 h, the mixture was diluted with 200 mL of THF and treated with a saturated aqueous solution of NH_4Cl . The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 . The combined organic solution was dried over MgSO_4 and the solvent was removed under reduced pressure. Recrystallization from CHCl_3 (0.471 g) and purification using preparative GPC eluted with CHCl_3 (0.143 g) gave **10** (81.7%) as a colorless solid: mp 270.1–271.7 °C; ^1H NMR (CDCl_3) δ 3.23 (m, 2H), 3.10 (m, 2H), 1.78 (m, 8H), 1.43 (m, 8H); ^{13}C NMR (CDCl_3) δ 145.2, 142.9, 124.1, 101.7, 30.4, 30.3, 26.0, 25.6; EI MS m/z 482 (M^+); HRMS calcd for $\text{C}_{20}\text{H}_{20}\text{Br}_2\text{S}_2$, 481.9373, found 481.9391. Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{Br}_2\text{S}_2$: C, 49.60; H, 4.16. Found: C, 49.38; H, 4.11.

Quarterthiophene 1(4T). A solution of dibromobithiophene **10** (0.100 g, 0.207 mmol), 2-stannylthiophene **9** (0.137 g, 0.419 mmol), $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (0.0231 g, 0.0223 mmol), and tri(2-furyl)phosphine (0.0444 g, 0.191 mmol) in 50 mL of dry THF was stirred at 50 °C for 5 days. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl , extracted with ether, and dried over MgSO_4 . The volatiles were removed in vacuo and the residue was purified by preparative GPC eluted with CHCl_3 to afford **1(4T)** (0.0624 g, 46.3%) as a yellow solid: mp 317.7–322.0 °C (dec); UV–vis (CH_2Cl_2) λ_{max} 225 nm ($\log \epsilon$ 4.04), 258 (4.11), 372 (4.37); ^1H NMR (CD_2Cl_2) δ 6.95 (s, 2H), 3.54 (m, 2H), 3.40 (m, 2H), 3.25 (m, 2H), 3.18 (m, 2H), 1.74 (m, 16H), 1.51 (m, 8H), 1.40 (m, 8H); ^{13}C NMR (CD_2Cl_2) δ 144.4, 143.4, 141.2, 139.9, 131.0, 126.4, 122.5, 122.0, 31.3, 31.3, 30.4, 30.4, 27.4, 26.9, 26.2, 26.1; EI MS m/z 650 (M^+); HRMS calcd for $\text{C}_{40}\text{H}_{42}\text{S}_4$, 650.2169; found, 650.2165.

Sexithiophene 1(6T). A solution of *n*-butyllithium in hexane (1.60 M, 0.130 mL, 0.208 mmol) was added dropwise to a stirred solution of dibromobithiophene **10** (0.100 g, 0.207 mmol) in THF (50 mL) at –78 °C over 1 min. After 30 min, the reaction mixture was quenched with water, extracted with CH_2Cl_2 , and dried over MgSO_4 . The volatiles were removed in vacuo to afford bromobithiophene **11** (0.0815 g, 97.3%) as a

colorless solid: ^1H NMR (CDCl_3) δ 6.85 (s, 1H), 3.28 (m, 2H), 3.12 (m, 1H), 3.07 (m, 1H), 1.80 (m, 8H), 1.48 (m, 8H); ^{13}C NMR (CDCl_3) δ 146.1, 145.1, 142.7, 142.2, 125.4, 123.4, 113.9, 101.1, 31.6, 30.3, 30.0, 26.3, 26.0, 26.0, 25.6, 25.5. A solution of bromobithiophene **11** (0.217 g, 0.535 mmol), 2-stannylthiophene **9** (0.176 g, 0.537 mmol), $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (0.0143 g, 0.0138 mmol), and tri(2-furyl)phosphine (0.0288 g, 0.124 mmol) in 150 mL of dry THF was stirred at 60 °C for 28 h. The reaction mixture was quenched with water, extracted with CH_2Cl_2 , and dried over MgSO_4 . The volatiles were removed in vacuo, and the residue was purified by flash chromatography over SiO_2 with CH_2Cl_2 as an eluent and by preparative GPC eluted with toluene to give crude **12** (0.170 g, 65.0%) as a yellow solid: ^1H NMR (CD_2Cl_2) δ 6.96 (s, 1H), 6.87 (s, 1H), 3.52 (m, 1H), 3.32 (m, 1H), 3.27 (m, 2H), 3.21 (m, 1H), 3.07 (m, 1H), 1.81 (m, 12H), 1.44 (m, 12H); ^{13}C NMR (CD_2Cl_2) δ 147.0, 145.2, 144.0, 143.0, 141.9, 140.7, 131.3, 127.0, 124.8, 123.3, 122.6, 114.2, 32.3, 32.0, 32.0, 31.1, 30.9, 30.8, 28.0, 27.5, 27.0, 26.9, 26.7, 26.7; HRMS calcd for $\text{C}_{30}\text{H}_{32}\text{S}_3$, 488.1666, found 488.1660. Into 100 mL of CH_2Cl_2 were dissolved crude **12** (0.108 g, 0.220 mmol) and $\text{NO}^+\text{SbF}_6^-$ (0.126 g, 0.472 mmol) with stirring at room temperature. After the resulting dark blue solution was stirred for 7 h, tetrabutylammonium iodide (1.38 g, 3.74 mmol) was added to the solution in one portion. The crude mixture was washed with a saturated aqueous solution of NaHCO_3 (50 mL), extracted with CH_2Cl_2 , and dried over MgSO_4 . The volatiles were removed in vacuo, and the residue was purified by flash chromatography over SiO_2 with CH_2Cl_2 as an eluent and by preparative GPC eluted with toluene to give **1(6T)** (0.0868 g, 80.9%) as a yellow solid: mp 218.7–220.5 °C (dec); UV–vis (CH_2Cl_2) λ_{max} 225 nm ($\log \epsilon$ 4.28), 260 (4.28), 383 (4.54); ^1H NMR (C_6D_6) δ 7.13 (s, 2H), 3.66 (m, 2H), 3.59 (m, 2H), 3.56 (m, 2H), 3.52 (m, 2H), 2.99 (m, 4H), 1.51 (m, 40H), 1.27 (m, 8H); ^{13}C NMR (C_6D_6) δ 145.1, 144.5, 144.3, 144.2, 142.4, 140.8, 132.0, 125.6, 125.1, 123.5, 123.2, 123.2, 32.0, 31.3, 28.0, 27.6, 26.9, 26.9, 26.8; EI MS m/z 974 (M^+); HRMS calcd for $\text{C}_{60}\text{H}_{62}\text{S}_6$, 974.3176, found 974.3168.

X-ray Structural Analysis. Intensity data were collected at 100 K on a Bruker SMART APEX diffractometer with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å) and graphite monochromator. The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares on F^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions.

1(2T): Single crystals suitable for X-ray crystallography were obtained by recrystallization from toluene. A disordered solvent molecule (toluene) was included in the lattice, and the occupancies of disordered toluene moieties were refined as 0.72:0.28. The sulfur atoms and unsubstituted β -carbon atoms in both of thiophene rings were also disordered and the occupancies of the disordered atoms were refined as 0.58:0.42, assuming that the conformation in the solid state is transoid. $\text{C}_{27}\text{H}_{30}\text{S}_2$; FW = 418.63, crystal size $0.30 \times 0.30 \times 0.30$ mm³, triclinic, $P-1$, $a = 6.3159(6)$ Å, $b = 10.5969(10)$ Å, $c = 16.9425(17)$ Å, $\alpha = 74.183(2)^\circ$, $\beta = 88.992(2)^\circ$, $\gamma = 85.741(2)^\circ$, $V = 1087.99(18)$ Å³, $Z = 2$, $D_c = 1.278$ g cm^{–3}. The refinement converged to $R_1 = 0.0536$, $wR_2 = 0.1490$ ($I > 2\sigma(I)$), GOF = 1.049.

1(3T): Single crystals suitable for X-ray crystallography were obtained by recrystallization from toluene. The terminal thiophene rings were disordered and the occupancies of (S1, C3 and S3, C11) and (S3, C10 and S33, C50) were refined as 0.81:0.19 and as 0.84:0.16, respectively. $\text{C}_{30}\text{H}_{32}\text{S}_3$; FW = 488.74, crystal size $0.20 \times 0.20 \times 0.10$ mm³, monoclinic, $P2_1(1)/n$, $a = 13.1988(8)$ Å, $b = 10.1717(7)$ Å, $c = 17.8654(11)$ Å, $\beta = 96.436(2)^\circ$, $V = 2383.4(3)$ Å³, $Z = 4$, $D_c = 1.362$ g cm^{–3}. The refinement converged to $R_1 = 0.0392$, $wR_2 = 0.0845$ ($I > 2\sigma(I)$), GOF = 0.924.

10: Single crystals suitable for X-ray crystallography were obtained by recrystallization from hexane. $\text{C}_{20}\text{H}_{20}\text{Br}_2\text{S}_2$; FW = 484.30, crystal size $0.20 \times 0.20 \times 0.20$ mm³, triclinic, $P-1$, $a = 8.5907(18)$ Å, $b = 9.505(2)$ Å, $c = 12.059(3)$ Å, $\alpha = 93.242-$

(4)°, $\beta = 107.154(4)^\circ$, $\gamma = 102.644(4)^\circ$, $V = 910.3(3) \text{ \AA}^3$, $Z = 2$, $D_c = 1.767 \text{ g cm}^{-3}$. The refinement converged to $R_1 = 0.0622$, $wR_2 = 0.1648$ ($I > 2\sigma(I)$), GOF = 0.958.

Cyclic Voltammetry. Cyclic voltammetry (CV) at room temperature was performed using a standard three-electrode cell consisting of a glassy-carbon working electrode, a Pt-wire counter electrode, and a Ag/AgNO₃ reference electrode under argon atmosphere. For the measurements under vacuum at -78°C , a homemade CV cell consisting of three Pt wires as a working electrode, a counter electrode, and a pseudo-reference electrode was used. The measurements were conducted for 1 mM solutions of samples in CH₂Cl₂ with tetrabutylammonium hexafluorophosphate as a supporting electrolyte (0.1 M). The potentials were calibrated with ferrocene as an internal standard.

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Supporting Information Available: ¹H and ¹³C NMR spectra of **1**, **8**, and **9**; X-ray crystallographic data for crystals **1**(2T), **1**(3T), and **10**; and Cartesian coordinates and total energies for the optimized structures of all calculated molecules. This materials is available free of charge via the Internet at <http://pubs.acs.org>.

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