Synthesis and Structural, Electronic, and Optical Properties of Oligo(thienylfuran)s in Comparison with Oligothiophenes and Oligofurans

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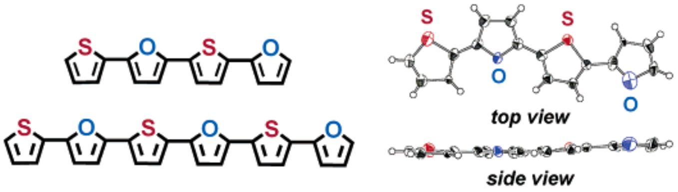

Alternate thiophene/furan oligomers having four and six heterocycles, i.e., oligo(thienylfuran) dimer and trimer **2** ($n = 4$ and 6), were newly synthesized by repetitive Stille coupling reactions. The structural, electronic, and optical properties of these oligomers were investigated by X-ray crystallography (for $n = 4$), cyclic voltammetry (CV), UV−vis and fluorescence spectroscopy, and DFT calculations, and the results were compared with those of corresponding oligothiophenes (**1**) and oligofurans (**3**). The inter-ring torsional energy profiles calculated for bithiophene **1** ($n = 2$), thienylfuran **2** ($n = 2$), and bifuran **3** ($n = 2$) at the B3LYP/6-31G(d) level indicated that the most stable conformers of **2** ($n = 2$) and **3** ($n = 2$) are fully coplanar with transoid structure while that of **1** ($n = 2$) is twisted with a dihedral angle of 158°. In accord with this, X-ray crystallographic analysis of **2** ($n = 4$) revealed that the π-conjugated system is nearly planar with the inter-ring C═C−C═C dihedral angles between the thiophene and furan rings of 173.6(7)°, −177.0(7)°, and 172.6(6)°. In the packing structure, these nearly planar molecules are arranged in a herringbone pattern. The CV on a series of oligo(thienylfuran)s **2** showed irreversible oxidation peaks at +0.90, +0.42, and +0.29 V vs Fc/Fc$^+$ for $n = 2$, 4, and 6, which were 0.15−0.18 V lower than those for corresponding oligothiophenes **1** and were closer to those for oligofurans **3**. On the other hand, the UV−vis spectra of **2** showed the longest wavelength absorption to be almost identical with those of the corresponding **1**, and more bathochromically shifted than those of the corresponding **3**. The results of CV and UV−vis measurements were supported by DFT calculations (B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d)). Thus, oligo(thienylfuran)s **2** have HOMOs which are higher than those of oligothiophenes **1** and close to those of **3**, and HOMO-LUMO gaps which are close to those of **1** and smaller than those of **3**. In fluorescence spectra, the quantum yield of **2** increased with elongation of the π-system ($n = 2$ (3.5%), 4 (19%), 6 (24%)).

Introduction

Oligothiophenes have attracted considerable attention as the active component of organic electronic devices.[1−3] Particularly, α-oligothiophenes (**1**) and their α-alkylated derivatives are among the most intensively investigated organic materials for light-emitting diodes (LED)[2] and field-effect transistors (FET).[2−5] For construction of these devices with oligothiophenes **1** ($n = 6$ and 8), which are the well-investigated oligothiophenes, high-vacuum depo-

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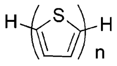
sition is typically utilized because of their insolubility. The improvement of solubility of these organic materials is quite important because it can provide the possibility of low-cost processing of thin films by spin coating[4] and inkjet printing.[5] The introduction of appropriate substituents to thiophene rings is one approach to increase the solubility of oligothiophenes, and recently high-performance FETs have been demonstrated by using such soluble oligo-[4d] and polythiophenes.[4b,e] As another approach, replacement of sulfur atoms of some of the thiophene units by other heteroatoms may also be useful.

As such, mixed π-conjugated oligomers made of thiophenes and other five-membered heterocycles such as furan,[6] pyrrole,[6e,7] silole,[8] and phosphole[9] have recently been investigated. Hucke and Cava have synthesized oligomers composed of alternately connected furan and thiophene rings, but their detailed properties have not been fully examined except for UV−vis and electrochemical data.[6c] Compared with oligothiophenes **1**, the solubility of these furan-containing oligomers is significantly enhanced. Therefore, further comparison of the structural and electronic properties of these "heterooligomers" with "homooligomers" such as oligothiophene **1** and oligofuran **3** appears important to explore the potential of these oligomers for the use in electronic devices. The mixed thiophene/furan oligomers so far reported consist of an odd number of five-membered rings,[6c] and no series of oligomers with an even number has been reported.



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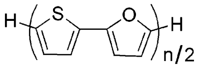

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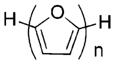

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In this paper, we report synthesis and fundamental electronic properties of oligo(thienyfuran)s **2** with an even number of five-membered-ring heterocycles ($n = 2, 4, 6$). These were synthesized by repetitive oligomerization, using Stille cross-coupling reactions. Then, the structural features and electronic and optical properties, including absorption and emission, as well as redox properties, were investigated by means of X-ray crystallographic study, theoretical calculations, cyclic voltammetry, and UV−vis and fluorescence spectroscopy. The results are discussed in comparison with the properties of corresponding oligothiophenes **1** and oligofurans **3**.

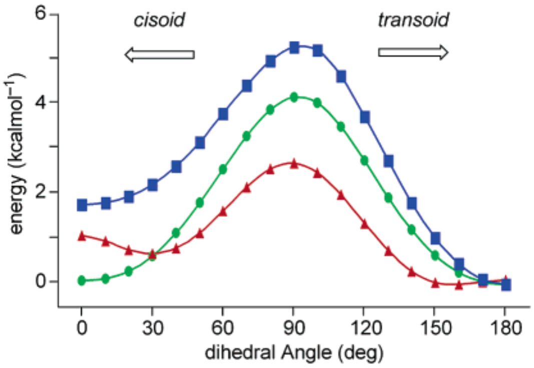

FIGURE 1. Inter-ring torsional energy profiles for **1** ($n = 2$) (red), **2** ($n = 2$) (green), and **3** ($n = 2$) (blue) (B3LYP/6-31G-(d)).

Results and Discussion

Synthesis. In general, the functionalization involving halogenation and lithiation of the C−H bonds at the α-position in the π-conjugated oligomers of five-membered heterocycles becomes less regio-selective with extension of the chain length.[6c,10] Thus, a TMS group was used to protect one side for the selective bromination of the other and also as a "tag" for selective iodination at this position.[11]

As shown in Scheme 1, silylated thienylfuran **5** prepared by Stille coupling of 2-bromo-5-(trimethylsilyl)-thiophene[12] with 2-(trimethylstannyl)furan[13] in the presence of copper(II) oxide[14] was brominated by NBS in the presence of a catalytic amount of benzoyl peroxide (BPO) in toluene to give **6** ($n = 2$) in 92% yield. Then, the TMS group of **6** ($n = 2$) was transformed into an iodo group with ICl to give **7**, while the bromo group of **6** ($n = 2$) was transformed into a stannyl group by lithiation followed by addition of trimethyltin chloride to give **8** ($n = 2$). Iodide **7** was quite unstable and was immediately used in the next cross-coupling reaction without purification. The cross-coupling reaction of **7** and **8** was carried out without copper(II) oxide, because the reaction was, otherwise, too fast to be controlled for the selective formation of **6** ($n = 4$). Debromination and desilylation of **6** ($n = 4$) afforded thienylfuran dimer **2** ($n = 4$) as a yellow solid. By the coupling reaction carried out similarly above, **6** ($n = 6$) was synthesized in 37% yield, from which was obtained thienylfuran trimer **2** ($n = 6$) as an orange solid by debromination and desilylation.

In contrast to the intractably low solubility of oligothiophene **1** ($n = 6$), oligo(thienylfuran) **2** ($n = 6$) is readily

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SCHEME 1

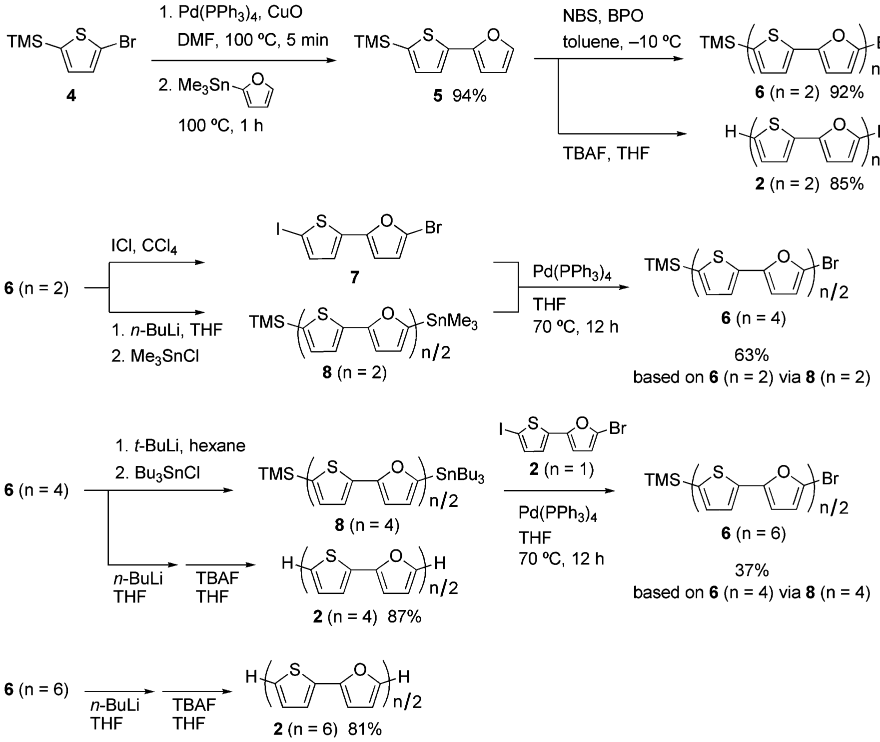

TABLE 1. Comparison of the Main Features of Torsional Energy Profiles for 1 (n = 2), 2 (n = 2), and 3 (n = 2)[a]

	dihedral angle (deg)		energy (kcal mol^{-1})		
				energy barrier	
compd	cis	trans	trans relative to cis	cis to trans	trans to cis
1 (n = 2)	30	158	−0.7	2.0	2.7
2 (n = 2)	0	180	−0.1	4.1	4.2
3 (n = 2)	0	180	−1.8	3.5	5.3

[a] B3LYP/6-31G(d).

TABLE 2. KS HOMO and LUMO Levels and HOMO-LUMO Gaps[a]

compd	HOMO (eV)	LUMO (eV)	HOMO-LUMO gap (eV)
1 (n = 2)	−5.84	−1.60	4.24
1 (n = 4)	−5.28	−2.24	3.04
1 (n = 6)	−5.10	−2.47	2.63
2 (n = 2)	−5.69	−1.43	4.26
2 (n = 4)	−5.14	−2.04	3.10
2 (n = 6)	−4.96	−2.26	2.70
3 (n = 2)	−5.62	−1.12	4.50
3 (n = 4)	−5.07	−1.76	3.31
3 (n = 6)	−4.89	−1.99	2.90

[a] B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d).

soluble in common organic solvents such as dichloromethane and benzene in a concentration of approximately 20 mg/mL or slightly higher. Also, melting points of **2** (n = 4 (76.5−77.0 °C) and 6 (143.4−144.7 °C)) are significantly lower than those of corresponding oligothiophenes **1** (n = 4 (208−210 °C) and 6 (302−307 °C)).[15]

Theoretical Calculations. To predict differences in the structural and electronic properties of **1**, **2**, and **3**, theoretical calculations were carried out at the B3LYP/6-31G(d) level. First, the inter-ring torsional energy profiles of **1**−**3** (n = 2) were obtained by calculating the energy for each conformer upon changing the inter-ring C=C−C=C torsion angle by 10° (Figure 1). From the results shown in Figure 1 and Table 1, the most stable conformer of **2** (n = 2) and **3** (n = 2) is found to be the one with fully coplanar and transoid structure, while that of **1** (n = 2) is twisted with the optimized dihedral angle of 158° (Table 1). This twisting of **1** (n = 2) is ascribed to the steric repulsion between the sulfur atom and a β-hydrogen of the adjacent thiophene ring. Also, the dihedral angles of the most stable cisoid conformers of **1** (n = 2), **2** (n = 2), and **3** (n = 2) are 30°, 0°, and 0°, respectively. Again, only **1** (n = 2) is not planar due to the same steric reason. These results are in reasonable agreement with the recent report on calculations for **1** (n = 2) and **2** (n = 2) at the HF/6-31G(d,p) level.[16]

Next, Kohn−Sham (KS) HOMO and LUMO levels, and the HOMO-LUMO gaps of **1**−**3** (B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d)), were calculated to give the results summarized in Table 2. Upon comparison of analogues with the same number of rings, the HOMO levels of oligo(thienylfuran)s **2** are higher than those of corresponding thiophenes **1** by 0.14−0.15 eV, while the values for oligofurans **3** are higher than those of **2** by 0.07 eV. The donor abilities of **2** and **3** are predicted to be higher than that of **1**. On the other hand, the HOMO-LUMO gap of **2** is quite close to that of **1**, while it is smaller than that of **3** by 0.20−0.24 eV. This implies that the excitation

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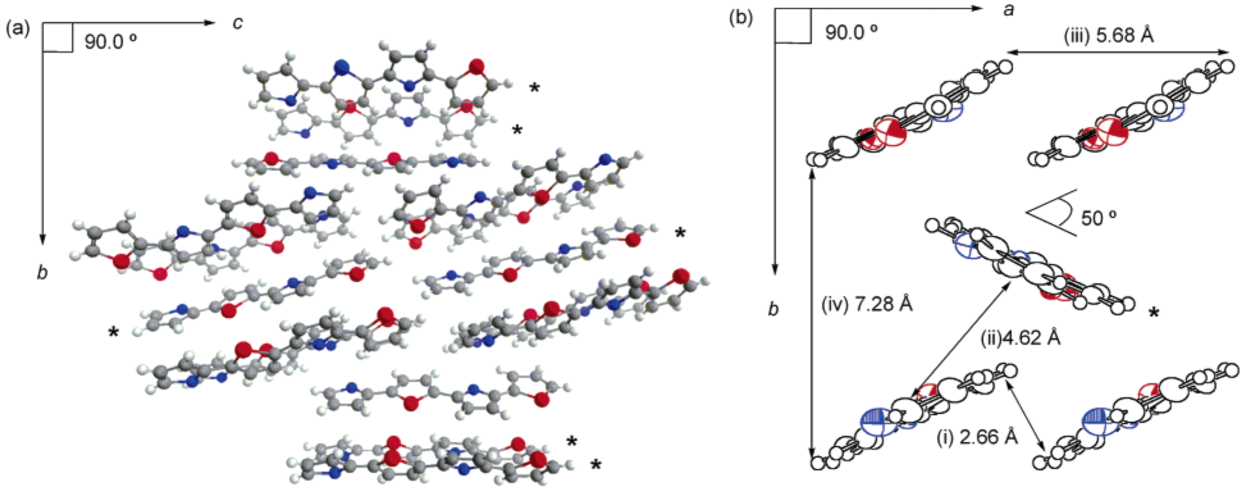

FIGURE 2. (a) Packing structure within the *bc* plane of **2** ($n = 4$). (b) The herringbone angle and the intermolecular distances within the *ab* plane of **2** ($n = 4$). One of the disordered molecules is shown by an asterisk. Sulfur and oxygen atoms are shown in red and blue, respectively.

energy of **2** is comparable to that of **1** and is smaller than that of **3**.

Crystal Structure of Thienylfuran Dimer 2 ($n = 4$). Recently, a considerable number of single crystals of oligothiophenes were successfully obtained by sublimation under a very low pressure of inert gas and their X-ray structures were determined.[2,17] Similarly, the single crystals of **2** ($n = 4$) were obtained by sublimation at 80 °C under a reduced pressure of nitrogen (ca. 3 mmHg) for 10 days, using an apparatus reported by Azumi and co-workers.[17e] The crystal structure of **2** ($n = 4$) was determined by X-ray crystallography at −173 °C. The ORTEP drawing exhibited an all-transoid and highly planar structure (see Supporting Information). The torsion angles (C3−C4−C5−C6, C7−C8−C9−C10, and C11−C12−C13−C14) between thiophene and furan rings were found to be 173.6(7)°, −177.0(7)°, and 172.6(6)°, respectively.

In the crystal packing structure shown in Figure 2, the molecules marked with an asterisk involved the statistical disorder along the long axis of the molecule. However, the disordered molecules are on the same plane, and the packing structure is in a herringbone arrangement similar to the case of oligothiophenes[17,18] as well as pentacene,[18] which has shown the best FET performance so far.[19] Figure 2b illustrates the herringbone packing of **2** ($n = 4$) within an *ab* plane of the crystal together with values of the herringbone angle and the intermolecular distances.[18,20] The observed herringbone angle (50°) and the intermolecular distances ((i) the distance between planes is 2.66 Å, (ii) the distance between the center of molecules is 4.62 Å, (iii) the intermolecular distance along the *a* axis is 5.68 Å, and (iv) the intermolecular distance along the *b* axis is 7.28 Å) of **2** ($n = 4$) are smaller than those of pentacene (53°, (i) 2.63 Å, (iii) 6.27 Å, and (iv) 7.78 Å)[18] and of **1** ($n = 6$) (65°, (i) 3 Å, (ii) 4.9 Å, (iii) the intermolecular distance along the *b* axis is 6.0 Å, and (iv) the intermolecular distance along the *c* axis is 7.9 Å),[18] indicating a more densely packed structure of **2** ($n = 4$). In fact, the shortest intermolecular contacts between heavy atoms were shown to be 3.32 Å between C6 and C8 of the adjacent molecules and 3.35 Å between C7 and C8 of the adjacent molecules, both of which are shorter than the sum of the van der Waals radii of sp^2-carbon atoms (3.40 Å). This distance is even smaller than the shortest intermolecular heavy atom contact in the crystal structures of **1** ($n = 4$) (C−S, 3.58 Å).[17c] Thus, replacement of some of the sulfur atoms of oligothiophene by smaller oxygen atoms seems to cause denser packing, which would be advantageous for effective electron transfer.

Electrochemistry. It has been reported that oligofurans **3** have lower oxidation potentials than oligothiophenes **1** of the corresponding sizes, indicating that HOMO levels of **3** are higher than those of **1**.[21] Then, the cyclic voltammetry (CV) of oligo(thienylfuran)s **2** was carried out in CH_2Cl_2 to compare their oxidation potentials with those of **1** and **3**. As summarized in Table 3, the CV of **2** ($n = 2, 4, 6$) showed irreversible oxidation peaks at the potential of +0.90, +0.42, and +0.29 V vs Fc/Fc$^+$, respectively, which are 0.15−0.18 V lower than the oxidation potentials of **1** of the corresponding sizes. Although care must be taken because of the difference of the solvent and reference electrode,[21,22] there seems to be a tendency that the oxidation potentials of **2** ($n = 4$ and 6) are rather closer to the values for **3** ($n = 4$ and 6) than those of **1**. This tendency is in agreement with the result of DFT calculations shown in Table 2. Hucke and Cava have reported that an oligomer with a thiophene

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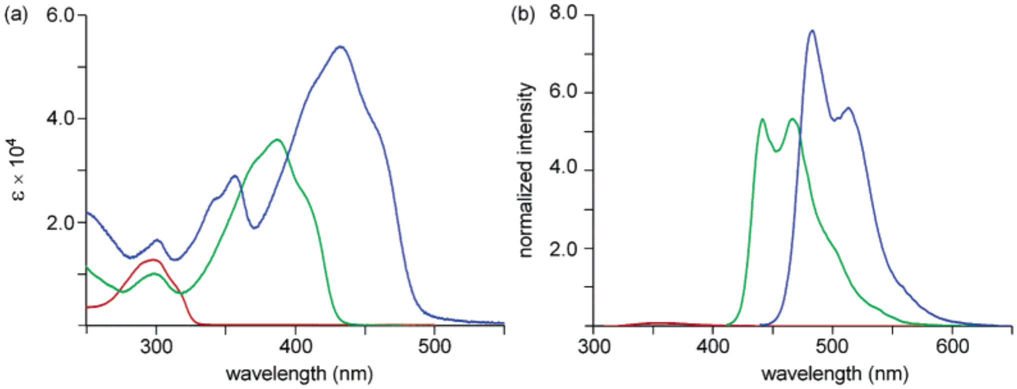

FIGURE 3. (a) Electronic absorption spectra and (b) fluorescence spectra of **2** (n = 2 (red), 4 (green), and 6 (blue)) measured in THF.

TABLE 3. Oxidation Potential (E_{pa}), Longest Wavelength Absorption (λ_{ab}), and Fluorescence Wavelength (λ_{em}) of 1, 2, and 3

compd	E_{pa} (V)[a]	λ_{ab} (nm)	λ_{em} (nm)
1 ($n = 2$)	+1.05[b]	302[c]	362[d]
1 ($n = 4$)	+0.60[b]	390[c]	437, 478[d]
1 ($n = 6$)	+0.45[e]	432[c]	469,[f] 510[d,f]
2 ($n = 2$)	+0.90[b]	298[g]	354, 358[g]
2 ($n = 4$)	+0.42[b]	387[g]	431, 457[g]
2 ($n = 6$)	+0.29[b]	432[g]	484, 514[g]
3 ($n = 2$)	+0.67[h]	282[i]	298, 313[i]
3 ($n = 4$)	+0.44[h]	361[i]	391, 413[i]
3 ($n = 6$)	+0.36[e]	399[f]	436,[f] 463[f]

[a] V vs Fc/Fc$^+$. [b] In CH_2Cl_2. [c] In $CHCl_3$: ref 23. [d] In dioxane; ref 24. [e] Predicted value based on a 1/n vs E_{pa} plot. [f] Predicted value based on a 1/n vs E_{max} plot. [g] In THF. [h] Converted from the E vs SCE: refs 21 and 22. [i] In CH_3CN: ref 25.

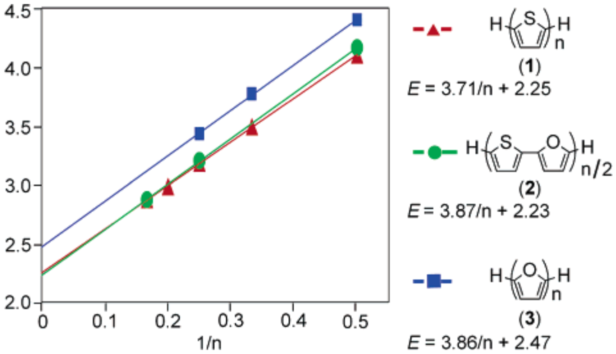

FIGURE 4. Correlation between electronic transition energies (E) and inverse ring numbers (1/n) of oligothiophene **1** (red),[23] oligo(thienylfuran) **2** (green), and oligofuran **3** (blue).[25]

ring connected to the furan terminus of **2** (n = 4) and an oligomer with a furan ring connected to the thiophene terminus of **2** (n = 4) exhibit reversible and irreversible oxidation peaks at $E_{1/2}$ +0.39 V and E_{pa} +0.35 V vs Fc/Fc$^+$, respectively (converted from the E vs SCE).[6c,22] These data demonstrate that oxidation potentials decrease with an increase in the number of furan rings. Qualitatively, oxidation potentials also decrease with an increase in the chain length of oligomers with both even and odd numbers of heterocycles. Thus, the irreversible oxidation peak potential mentioned above is located between the E_{pa} values for **2** (n = 4) (+0.42 V) and **2** (n = 6) (+0.29 V) observed in the present work.

Absorption and Fluorescence Spectra. The UV−vis absorptions of oligo(thienylfuran)s **2** exhibited clear bathochromic shift with increasing number of heterocycles as shown in Table 3 and in Figure 3a. The observed maximum absorptions are quite close to the values for corresponding oligothiophenes **1**, and bathochromically shifted by 16−33 nm as compared with those of oligofurans **3** of the corresponding ring numbers. These results indicate that HOMO-LUMO gaps of **2** are close to those of **1** and smaller than those of **3**, which is also consistent with the results of theoretical calculations (Table 2).

To compare the effectiveness of π-conjugation in **1**, **2**, and **3**, the values of E ($\pi-\pi^*$-transition energy) were plotted against 1/n (inverse ring number) to give the correlations shown in Figure 4. In this plot, a linear relationship is theoretically predicted[26] and the slope reflects the effectiveness of the π-conjugation, which involves structural factors such as bond alternation, planarity, and aromaticity.[27] In the case of oligo(thienylfuran)s **2**, a good linearity was observed, and the slope (3.87) was found to be slightly larger than that (3.71) for **1**, and almost equivalent to that (3.86) for **3**. This result suggests that the π-conjugation in **2** is slightly more effective than that in **1**. This would be ascribed to the lower aromaticity of furan than that of thiophene[28] and/or higher planarity of **2** than **1** as already mentioned above. On the other hand, if we assume that the linear plot can be extrapolated to 1/n = 0, the longest wavelength absorption for the poly(thienylfuran) with an infinite chain length could be predicted to appear at λ_{max} = 556 nm (2.23 eV).

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Some furan-containing oligomers and polymers are known to exhibit characteristic fluorescence.[29] We have examined the fluorescence spectra of **2** ($n = 2, 4, 6$), and the results are shown in Figure 3b. The maximum emission bands (λ_{em}) of **1**, **2**, and **3** are summarized in Table 3. According to the extension of the chain length, the quantum yields of **2** were found to increase ($n = 2$ (3.5%), 4 (19%), 6 (24%)). In particular, **2** ($n = 4$) and **2** ($n = 6$) emitted strong blue and green light, respectively.

Conclusion

In summary, a series of oligo(thienylfuran) **2** ($n = 2$, 4, and 6) were synthesized. The crystal structure of **2** ($n = 4$) revealed that the π-system is almost planar with more densely packed herringbone structure than that of oligothiophene **1** ($n = 4$). On the basis of the results of cyclic voltammetry and electronic spectral measurements, the HOMO levels of **2** were found to be close to those of oligofuran **3** and higher than those of **1** while the HOMO-LUMO gaps were shown to be close to those of **1** and smaller than those of **3**. These experimental observations are in qualitative agreement with the results of DFT calculations. Also it is to be noted that the solubility of **2** ($n = 6$) in common solvents is much better than that of **1** ($n = 6$). Thus, it is interesting to study the FET character of **2** ($n = 4, 6$), particularly because of the denser packing of **2** ($n = 4$), higher donor ability, and better solubility than **1**. The investigation into fabrication and evaluation of such devices with oligo(thienylfuran)s is currently underway.

Experimental Section

General Procedure. All reactions were carried out under an argon atmosphere unless otherwise noted. THF was distilled from sodium benzophenone ketyl. Hexane was distilled over sodium metal. Dichloromethane, carbon tetrachloride, and DMF were distilled over CaH_2. One drop of Et_3N was added to all solvents used for the workup procedures. All commercially available materials were of reagent grade unless otherwise noted. 2-Bromo-5-(trimethylsilyl)thiophene[12] and 2-(trimethylstannyl)furan[13] were synthesized according to literature procedure.

Computational Method. All calculations were conducted with the Gaussian 98 programs.[30] Geometry optimization and calculations on inter-ring torsional energy profiles were performed with the restricted Becke hybrid (B3LYP) at the 6-31G(d) level. The HOMO and LUMO levels were estimated at single-point calculations (B3LYP/6-311+(2d,p)), using the geometries optimized at the B3LYP/6-31G(d) levels.

2-{2-(5-trimethysilyl)thienyl}furan (5). A mixture of 2-bromo-5-(trimethylsilyl)thiophene[12] (5.47 g, 23.4 mmol), $Pd(PPh_3)_4$ (1.35 g, 1.17 mmol), and CuO (1.86 g, 23.4 mmol) in 60 mL of DMF was stirred at 100 °C.[14] After 5 min, a solution of 2-(trimethlstannyl)furan[13] (7.56 g, 32.7 mmol) in 5 mL of DMF was added via a cannula. The mixture was stirred at 100 °C for 1 h and then cooled to room temperature. The precipitates were filtered off, and the volatiles of the filtrate were removed in vacuo. The residue was purified by flash chromatography over SiO_2 with hexane as an eluent to afford **5** (4.91 g, 94.4%) as a colorless oil: ^1H NMR (C_6D_6) δ 7.30 (d, 1H, $J = 3.5$ Hz), 7.02 (dd, 1H, $J = 2.1, 0.9$ Hz), 6.99 (d, 1H, $J = 3.5$ Hz), 6.35 (dd, 1H, $J = 3.3, 0.9$ Hz), 6.07 (dd, 1H, $J = 3.3, 2.1$ Hz), 0.22 (s, 9H); ^{13}C NMR (C_6D_6) δ 150.5, 142.3, 139.7, 139.5, 135.4, 124.7, 112.3, 105.9, 0.23; HRMS (EI) calcd for $C_{11}H_{14}OSSi$ 222.0535, found 222.0544.

Thienylfuran Monomer 2 ($n = 2$). To a stirred solution of **5** (0.462 g, 2.08 mmol) in 30 mL of wet THF was added a THF solution of Bu_4NF (1.0 M, 2.2 mL, 2.2 mmol) under air. The reaction mixture was stirred for 15 min, quenched by adding water (10 mL), and extracted with ether, and the organic layer was dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by column chromatography over SiO_2 with hexane as an eluent to afford **2** ($n = 2$) (0.266 g, 85.1%) as a colorless oil: ^1H NMR (C_6D_6) δ 7.11 (dd, 1H, $J = 3.5, 1.2$ Hz), 6.98−6.97 (m, 1H), 6.72−6.65 (m, 2H), 6.25 (d, 1H, $J = 3.3$ Hz), 6.03 (dd, 1H, $J = 3.3, 2.1$ Hz); ^{13}C NMR (C_6D_6) δ 150.3, 142.1, 134.6, 128.1, 124.7, 123.3, 112.2, 105.6. The ^1H and ^{13}C NMR spectral data were identical with those of commercially available reagent.

Compound 6 ($n = 2$). To a stirred solution of **5** (1.18 g, 5.32 mmol) and a small portion of benzoyl peroxide in toluene (30 mL) was gradually added NBS (0.95 g, 5.32 mmol) at −10 °C under air. After being stirred for 0.5 h at −10 °C, the mixture was evaporated under reduced pressure. The residue was subjected to flash chromatography over SiO_2 with hexane as an eluent to afford **6** ($n = 2$) (1.48 g, 92.3%) as a colorless solid: mp 37.2−38.0; ^1H NMR (C_6D_6) δ 7.16 (d, 1H, $J = 3.6$ Hz), 6.91 (d, 1H, $J = 3.6$ Hz), 6.07 (d, 1H, $J = 3.3$ Hz), 5.91 (d, 1H, $J = 3.3$ Hz), 0.20 (s, 9H); ^{13}C NMR (C_6D_6) δ 152.3, 140.0, 138.3, 135.4, 125.0, 121.8, 114.1, 108.1, 0.16; HRMS (EI) calcd for $C_{11}H_{13}BrOSSi$ 299.9640, found 299.9650.

Compoun 6 ($n = 4$). To a stirred solution of **6** ($n = 2$) (2.58 g, 8.5 mmol) in CCl_4 (70 mL) cooled at 0 °C was added a solution of iodine monochloride in CH_2Cl_2 (1.0 M, 8.6 mL, 8.6 mmol) dropwise over 20 min. The reaction mixture was stirred for 1 h at −10 °C and then for 4 h at room temperature. The reaction was quenched with a 10% aqueous solution of sodium thiosulfate (20 mL) and the mixture was extracted with dichloromethane. The organic layer was washed with brine and water and dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by flash chromatography over SiO_2 with hexane as an eluent to afford crude iodide **7** (2.37 g) as a yellow oil: ^1H NMR (C_6D_6) δ 6.68 (d, 1H, $J = 3.9$ Hz), 6.41 (d, 1H, $J = 3.9$ Hz), 5.80 (d, 1H, $J = 3.6$ Hz), 5.77 (d, 1H, $J = 3.6$). Because of the instability, the crude **7** was used in the next step without further purification.

A solution of *n*-butyllithium in hexane (1.60 M, 2.8 mL, 4.48 mmol) was added dropwise to a stirred solution of **6** ($n = 2$) (1.23 g, 4.08 mmol) in THF (50 mL) at −78 °C. After the mixture was stirred at −78 °C for 30 min, a THF solution of trimethyltin chloride (1.0 M, 4.9 mL, 4.9 mmol) was added. The reaction mixture was stirred at −78 °C for 1 h, and then at room temperature overnight. To this mixture, a solution of crude **7** in 20 mL of THF was added, followed by a solution of $Pd(PPh_3)_4$ (0.49 g, 0.43 mmol) in 20 mL of THF both added via cannula. The reaction mixture was stirred for 12 h at 70 °C. The solvent was removed in vacuo, and the residue was purified by column chromatography over SiO_2 eluted with hexane−CH_2Cl_2 (9:1) to afford **6** ($n = 4$) (1.16 g, 63.3%) as a yellow solid. An analytically pure sample was obtained by recrystallization from hexane: mp 100.1−100.5 °C; ^1H NMR

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(C_6D_6) δ 7.31 (d, 1H, J = 3.5 Hz), 7.03 (d, 1H, J = 3.5 Hz), 6.92 (d, 1H, J = 3.5 Hz), 6.86 (d, 1H, J = 3.5 Hz), 6.32 (d, 1H, J = 3.3 Hz), 6.22 (d, 1H, J = 3.3 Hz), 5.98 (d, 1H, J = 3.3 Hz), 5.90 (d, 1H, J = 3.3 Hz), 0.25 (s, 9H); ^{13}C NMR (C_6D_6) δ 151.8, 149.8, 148.9, 140.0, 139.1, 135.5, 133.0, 131.6, 124.9, 124.3, 123.9, 121.9, 114.2, 108.5, 108.3, 108.1, 0.24; HRMS (FAB) calcd for $C_{19}H_{17}BrO_2S_2Si$ 447.9623, found 447.9627. Anal. Calcd for $C_{19}H_{17}BrO_2S_2Si$: C, 50.77; H, 3.81. Found: C, 50.55; H, 3.87.

Thienylfuran Dimer 2 (*n* = 4). A solution of *n*-butyllithium in hexane (1.60 M, 0.8 mL, 1.28 mmol) was added dropwise to a stirred solution of **6** (n = 4) (0.52 g, 1.15 mmol) in THF (30 mL) at −78 °C. After the solution was stirred at −78 °C for 30 min, the reaction was quenched with water (10 mL), and the mixture was extracted with ether and dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was redissolved in 20 mL of wet THF. To the solution was added a solution of Bu_4NF in THF (1.0 M, 1.3 mL, 1.3 mmol) under air. The reaction mixture was stirred for 15 min, quenched with water (10 mL), and extracted with ether, and the organic layer was dried over $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by column chromatography over SiO_2 eluted with hexane−CH_2Cl_2 (20:1) to afford **2** (n = 4) (0.30 g, 87.4%) as a yellow solid. An analytically pure sample was obtained by recrystallization from hexane: mp 76.5−76.9 °C; ^1H NMR (C_6D_6) δ 7.12 (dd, 1H, J = 3.6, 1.5 Hz), 7.01−6.97 (m, 3H), 6.74−6.67 (m, 2H), 6.26−6.19 (m, 3H), 6.04 (dd, 1H, J = 3.3, 1.8 Hz); ^{13}C NMR (C_6D_6) δ 149.9, 149.5, 148.9, 142.3, 134.0, 133.0, 132.5, 128.3, 124.8, 124.0, 123.9, 123.5, 112.4, 108.2, 108.0, 106.0; HRMS (FAB) calcd for $C_{16}H_{10}O_2S_2$ 298.0122, found 298.0126. Anal. Calcd for $C_{16}H_{10}O_2S_2$: C, 64.35; H, 3.35. Found: C, 64.43; H, 3.82.

Compound 6 (*n* = 6). A solution of *tert*-butyllithium in hexane (1.42 M, 2.85 mL, 4.05 mmol) was added dropwise to a stirred solution of **6** (n = 4) (203.5 mg, 0.45 mmol) in hexane (30 mL) at 0 °C. After the solution was stirred for 3 h at 0 °C, tributyltin chloride (1.3 mL, 4.6 mmol) was added. The reaction mixture was stirred for 1 h at 0 °C, and then at room temperature overnight.

The solvent of the mixture was removed in vacuo. To this mixture, a solution of crude **7** (606 mg) in 20 mL of THF was added, followed by a solution of $Pd(PPh_3)_4$ (126.4 mg, 0.11 mmol) in 20 mL of THF both added via cannula. The reaction mixture was stirred for 17 h at 70 °C. The solvent was removed in vacuo, and the residue was purified by flash chromatography over SiO_2 eluted with hexane−CH_2Cl_2 (1:4). The eluted product was further purified by preparative GPC eluted with toluene to afford **6** (n = 6) (100.4 mg, 37.3%) as an orange solid. An analytically pure sample was obtained by reprecipitation from hexane and CH_2Cl_2: mp 147.0−147.6 °C; ^1H NMR (C_6D_6) δ 7.33 (d, 1H, J = 3.8 Hz), 7.04 (d, 2H, J = 3.8 Hz), 7.01 (d, 1H, J = 3.8 Hz), 6.90 (d, 1H, J = 3.8 Hz), 6.87 (d, 1H, J = 3.8 Hz), 6.35 (d, 1H, J = 3.6 Hz), 6.29 (d, 1H, J = 3.6 Hz), 6.22 (d, 1H, J = 3.6 Hz), 6.19 (d, 1H, J = 3.6 Hz), 5.98 (d, 1H, J = 3.6 Hz), 5.89 (d, 1H, J = 3.6 Hz), 0.25 (s, 9H); ^{13}C NMR (C_6D_6) δ 151.8, 149.8, 149.3, 149.1, 148.9, 140.5, 139.1, 135.5, 132.9, 132.8, 132.4, 131.7, 124.9, 124.4, 124.2, 124.1, 124.0, 121.9, 114.2, 108.6, 108.4, 108.3 108.2, 108,1, 0.25; HRMS (FAB) calcd for $C_{27}H_{21}BrO_3S_3Si$ 595.9605, found 595.9607. Anal. Calcd for $C_{27}H_{21}BrO_3S_3Si$: C, 54.21; H, 3.51. Found: C, 54.06; H, 3.81.

Thienylfuran Trimer 2 (*n* = 6). The procedures used for the synthesis of **2** (n = 4) were applied for the synthesis of **2** (n = 6). The use of **6** (n = 6) (220 g, 0.37 mmol), *n*-butyllithium in hexane (1.60 M, 0.25 mL, 0.4 mmol), and a THF solution of Bu_4NF (1.0 M, 0.40 mL, 0.40 mmol) gave **2** (n = 6) as an orange solid (140 mg, 84.7%). An analytically pure sample was obtained by reprecipitation from hexane and CH_2Cl_2: mp 143.4−143.7 °C; ^1H NMR (C_6D_6) δ 7.14 (dd, 1H, J = 3.5, 1.2 Hz), 7.02−6.99 (m, 5H), 6.75−6.68 (m, 2H), 6.28−6.20 (m, 5H), 6.06 (dd, 1H, J = 3.3, 1.8 Hz); ^{13}C NMR (C_6D_6) δ 149.9, 149.6, 149.1, 149.0, 142.4, 134.0, 133.2, 132.7, 132.5, 132.4, 129.2, 128.6, 128.3, 127.6, 124.9, 124.2, 124.1, 124.0, 123.6, 112.4, 108.4, 108.3, 108.1, 106.1; HRMS calcd (FAB) for $C_{24}H_{14}O_3S_3$ 446.0105, found 446.0101. Anal. Calcd for $C_{24}H_{14}O_3S_3$: C, 64.49; H, 3.14. Found: C, 64.08; H, 3.29.

X-ray Structural Analysis. Single crystals suitable for X-ray crystallography were obtained by sublimation at 80 °C under a reduced pressure of nitrogen (ca. 3 mmHg) for 10 days.[17e] Intensity data were collected at 100 K with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares on F^2 (SHELXL-97). Nonhydrogen atoms were refined anisotropically. All hydrogen atoms were placed by using AFIX instructions. The Z value of compound **2** (n = 4) is 6 in sprite of the monoclinic $P2_1/n$ space group because it has 1.5 nonidentical molecules in the unit cell. Although one of them was disordered in 1:1 ratio having a pseudocenter of symmetry in the middle of the disordered molecules, the disorder was solved adequately by using PART-1 instructions. The structural parameters of the disordered molecules were restrained to have geometries similar to each other by using SAME instruction. The anisotropic temperature factors of disordered molecules were restrained by using SIMU, DELU, and ISOR instructions. $C_{16}H_{10}O_2S_2$; FW = 298.36, crystal size 0.20 × 0.05 × 0.05 mm^3, monoclinic $P2_1/n$, a = 5.676(10) Å, b = 21.665(4) Å, c = 16.651(3) Å, β = 94.057(3)°, V = 2042.3(6) Å^3, Z = 6, D_c = 1.456 g cm^{-3}. The refinement converged to $R_1 = 0.0852$, w$R_2 = 0.2019$ ($I > 2\sigma(I)$), GOF = 1.094.

Cyclic Voltammetry. Cyclic voltammetry (CV) at room temperature was performed with use of a standard three-electrode cell consisting of a glassy-carbon working electrode, a Pt-wire counter electrode, and a Ag/$AgNO_3$ (CH_3CN) reference electrode under argon atmosphere. The CV measurements were carried out by using 1.0 mM solutions of samples with tetrabutylammonium perchlorate as the supporting electrolyte (0.1 M) in all measurements. The observed anodic peak potentials were calibrated with ferrocene added after each measurement.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of **5** and **6** (n = 2), and ^1H NMR spectrum of **7**; X-ray crystallographic data for crystals **2** (n = 4); and Cartesian coordinates and total energies for the optimized structures of all calculated molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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