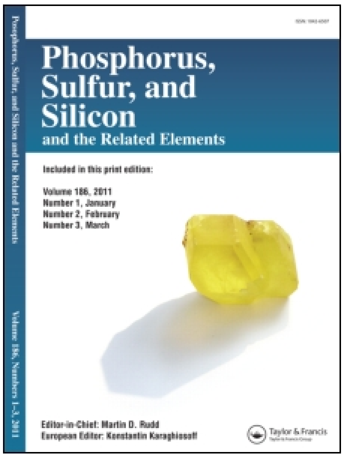

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Synthesis and Properties of Thienylene-Ethynylene-Tetrathiafulvalene Oligomers

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SYNTHESIS AND PROPERTIES OF THIENYLENE-ETHYNYLENE-TETRATHIAFULVALENE OLIGOMERS

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A series of thienylene-ethynylene-tetrathiafulvalene oligomers 1–6 have been synthesized by the Sonogashira reaction of iodo-tetrathiafulvalene derivatives with thienylethynes. The X-ray structure of 4,5-bis(2-thienylethynyl)tetrathiafulvalene (1b) revealed a planar structure of the molecule. The electronic spectra of neutral oligomers 1–6 suggest a partial intramolecular charge transfer between the TTF and thienylethyne units. The cyclic voltammetric measurements of 1–4 showed multi-redox processes.

Keywords Intramolecular CT-absorption; iodotetrathiafulvalenes; redox potential; Sonogashira reaction; tetrathiafulvalene; thienylacetylene

INTRODUCTION

(Arylene-ethynylene)-type conjugated oligomers are of considerable interest as materials for organic semiconductors, as nanostructured materials, and in the field of supramolecular chemistry.[1,2] In particular, (arylene-ethynylene) oligomers containing donor groups such as thiophene and tetrathiafulvalene (TTF) have been extensively studied for these applications.[3–15] Since the ethynylene unit has a high electron-withdrawing ability compared with π-donor groups, these oligomers have a potential to form low-bandgap oligomers. To explore such a property, we designed new redox active cooligomers **1**–**6** having thiophene, acetylene, and TTF units as shown in Figure 1. Previously, Yamamoto and Shimizu reported the linear copolymer of 2,5-thienylene, ethynylene, and 4,5′-TTF.[16] We report in this

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Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

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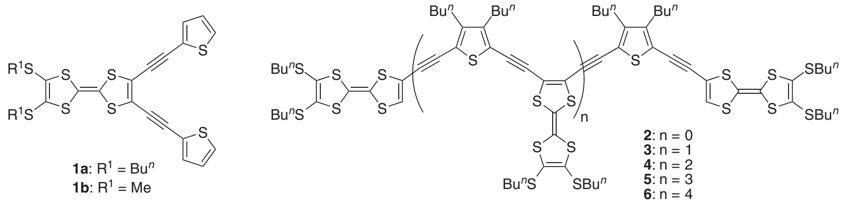
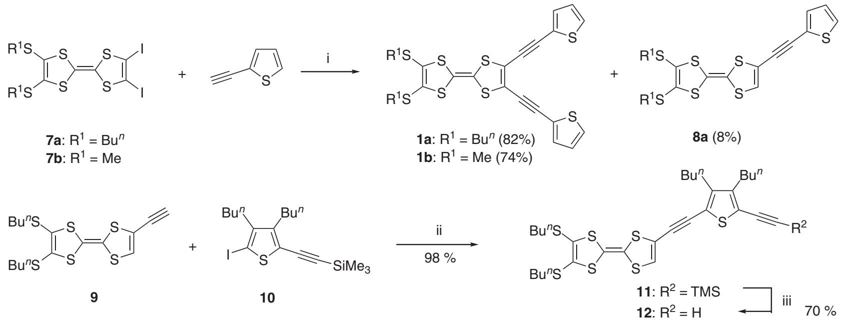


Figure 1 Oligomers composed of thiophene, acetylene, and TTF units.

article the synthesis and electronic properties of zigzag-type cooligomers **1–6** composed of 2,5-thienylene, ethynylene, and 4,5-TTF.

RESULTS AND DISCUSSION

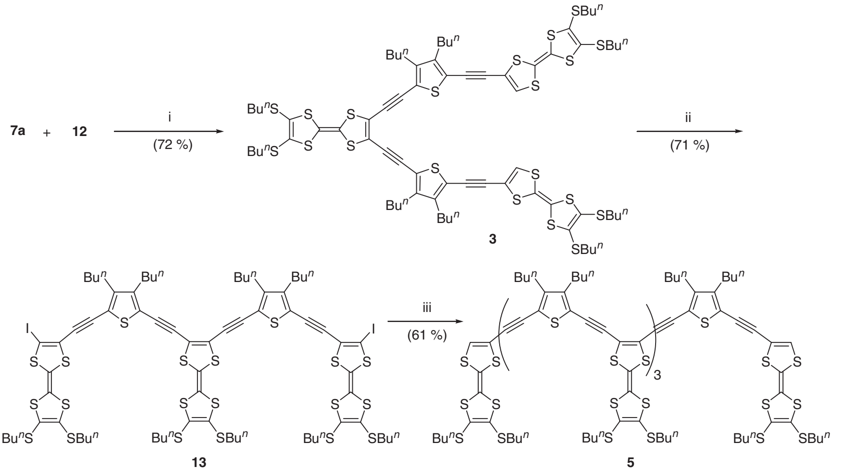
The synthesis of thienylene-ethynylene-TTF oligomers was carried out by the Sonogashira reaction of iodo-TTF derivatives with ethynylthiphene. Thus, 4,5-bis(2-thienylethynyl)tetrathiafulvalenes (**1a** and **1b**) were prepared by the reaction of 2-ethynlthiophene with diiodo-TTF **7** in the presence of CuI (20 mol%) and Pd(PPh$_3$)$_4$ (10 mol%) in 82% and 74% yields, respectively (Scheme 1). In the case of the reaction of **7a**, a small amount of monosubstituted **8a** was obtained in 8% yield. The precursor **12** was prepared by the Sonogashira reaction of 4′-ethynyl-4,5-bis(butylthio)tetrathiafulvalene **9** with 3,4-dibutyl-2-iodo-5-trimethylsilylethynylthiophene **10**, followed by deprotection of the trimethylsilyl group with K$_2$CO$_3$.



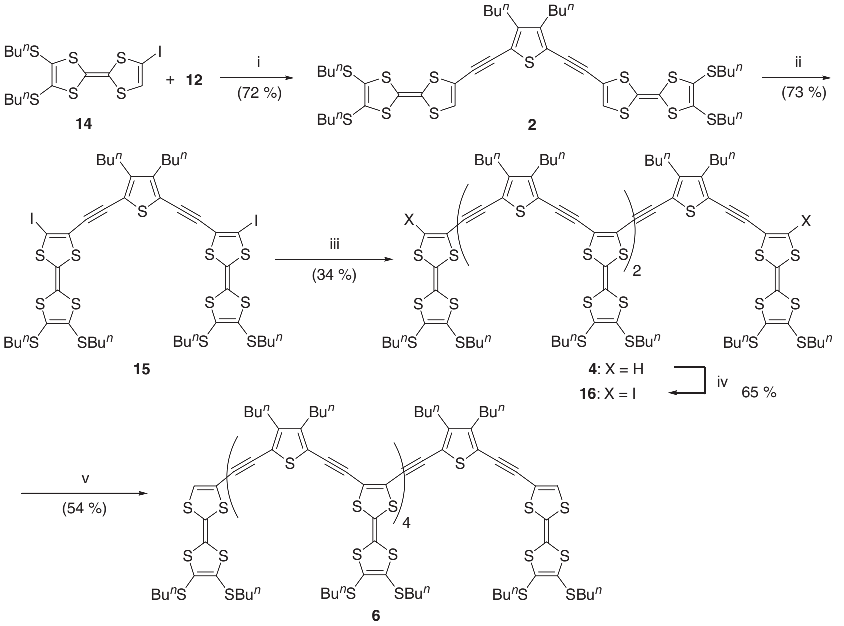
Scheme 1 Reagents and conditions: i) CuI (20 mol%), Pd(PPh$_3$)$_4$ (10 mol%), Et$_3$N-C$_6$H$_6$, rt, 15 h; ii) CuI (20 mol%), Pd(PPh$_3$)$_4$ (10 mol%), Et$_3$N-C$_6$H$_6$, rt, 6 h; iii) K$_2$CO$_3$, MeOH-THF, rt, 2 min.

The syntheses of the trimer **3** and the pentamer **5** were carried out as shown in Scheme 2. The reaction of **7a** with **12** in the presence of 50 mol% of CuI and 25 mol% of Pd(PPh$_3$)$_4$ in Et$_3$N and benzene gave the trimer **3a** in 72% yield. Further iodination was carried out by the addition of 3 equiv. of LDA into a mixture of **3** and C$_6$F$_{13}$I at –78 °C to afford **13** in 71% yield. The Sonogashira reaction of **13** with **12** under conditions similar to those used for the synthesis of the trimer **3** produced the pentamer **5** in 61% yield.

For the syntheses of the tetramer **4** and hexamer **6**, the dimer **2** was used as a key intermediate (Scheme 3). The dimer **2** was first prepared by the cross-coupling of 4′,5′-bis(butylthio)-4-iodotetrathiafulvalene **14** with **12** in 72% yield. The iodination of **2** with



Scheme 2 Reagent and conditions: i) CuI (50 mol%), $Pd(PPh_3)_4$ (25 mol%), Et_3N-C_6H_6, rt, 13 h; ii) $C_6F_{13}I$, LDA, THF, –78 °C, 14 h; iii) **12**, CuI (50 mol%), $Pd(PPh_3)_4$ (25 mol%), Et_3N-C_6H_6, rt, 13 h.



Scheme 3 Reagents and conditions: i) CuI (20 mol%), $Pd(PPh_3)_4$ (10 mol%), Et_3N-C_6H_6, rt, 6 h; ii) $C_6F_{13}I$, LDA, THF, –78 °C, 12 h; iii) **12**, CuI (50 mol%), $Pd(PPh_3)_4$ (25 mol%), Et_3N-C_6H_6, rt, 15 h; iv) $C_6F_{13}I$, LDA, THF, –78 °C, 14 h; v) **12**, CuI (50 mol%), $Pd(PPh_3)_4$ (25 mol%), Et_3N-C_6H_6, rt, 13 h.

$C_6F_{13}I$ and LDA produced the diiodide **15** in 73% yield. The palladium-catalyzed reaction of the diiodide **15** with **12** afforded the tetramer **4** in 34% yield. Further conversion of **4** to the hexamer **6** was carried out via the diiodide **16** in moderate yield. Although the Sonogashira reaction of the diiodides **7a**, **13**, **15**, and **16** with **12** in Et_3N and benzene at room temperature produced the desired oligomers **3**–**6** in moderate to good yields, the yield

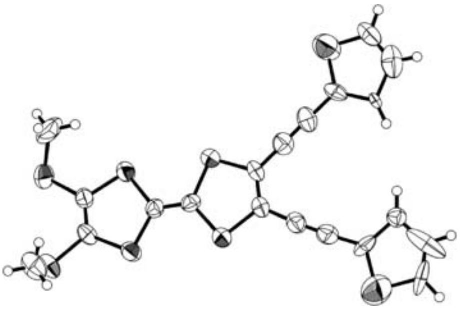


Figure 2 ORTEP drawing of **1b**.

decreased along with the elongation of chain length. All cooligomers **1–6** prepared are stable yellow to orange solids.

The structure of **1b** was confirmed by X-ray crystallographic analysis as shown in Figure 2.[17] The molecule **1b** adopts an almost planar structure except for the SMe groups. The terminal thiophene moieties are disordered in the crystal. The two thiophene-sulfur atoms face outside in the major conformation.

Table I summarizes the electronic absorption spectra of the oligomers **1a** and **2–6** together with **8a** in CH_2Cl_2. The spectrum of the monomer **1a** with two thienylethynes exhibits the π–π^* transition at 450 nm, although the monomer **8a** exhibits the corresponding absorption maximum at 416 nm. This bathochromic shift clearly indicates a partial intramolecular charge transfer between the TTF and thienylethyne units, together with the extension of π-conjugation. In fact, MO calculations of the monomer **1a** (B3LYP/6–31G) show that the HOMO of **1a** is mainly located on the TTF moiety, while the LUMO is mainly located on the thienylethyne moiety. Furthermore, distinct redshift of the π–π^* transition was observed with increasing chain length until the hexamer. Thus, the effective conjugation length of the thienylene-ethynylene-TTF oligomers is longer than the hexamer.

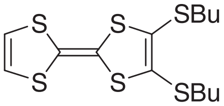
Cyclic voltammetric analyses of **1a** and **2–4** together with **8a** and **17** were carried out in PhCN (Table II). All cyclic voltammograms (CVs) showed only redox waves assigned to the TTF moieties. The CV of the monomer **1a** showed two reversible redox waves at 0.15 and 0.41 V (vs. Fc/Fc^+) corresponding to the formation of **1a**$^{\bullet+}$ and **1a**$^{2+}$, respectively. Similarly, the CV of **8a** also showed sequential oxidation to produce **8a**$^{\bullet+}$ and **8**$^{2+}$. The marked positive shift of $E_1{}^{1/2}$ of **1a** compared with **8a** suggests that thienylethyne groups

Table I Absorption maxima of the oligomers **1a** and **2–6** together with **8a**[a]

Compounds	λ_{max}
1a (monomer)	450 nm
8a (monomer)	416 nm
2 (dimer)	472 nm
3 (trimer)	506 nm (sh.)
4 (tetramer)	540 nm (sh.)
5 (pentamer)	575 nm (sh.)
6 (hexamer)	580 nm (sh.)

[a] Measured in dichloromethane at rt.

Table II Redox potentials of the oligomers **1a** and **2–4** together with **8a** and **17**[a]


17

	$E_1^{1/2}$	$E_2^{1/2}$	$E_3^{1/2}$
17	−0.09 (1e$^-$)	0.32 (1e$^-$)	
8a	0.08 (1e$^-$)	0.41 (1e$^-$)	
1a	0.15 (1e$^-$)	0.41 (1e$^-$)	
2	0.05 (2e$^-$)	0.40 (2e$^-$)	
3	0.03 (2e$^-$)	0.08 (1e$^-$)	0.37 (3e$^-$)
4	0.09 (2e$^-$)	0.19 (2e$^-$)	0.44 (2e$^-$)

[a] Conditions: $Bu^n_4NClO_4$, PhCN, Pt working electrode and counter electrode. Potentials were measured against a Ag/Ag$^+$ electrode and converted to the vales vs Fc/Fc$^+$.

can be regarded as electron-withdrawing groups against the TTF moiety. Thus, the $E_1^{1/2}$ value of the dimer **2** decreased compared with that of **8a** owing to the decrease in the number of the thienylethyne moieties. By the same reason, the $E_2^{1/2}$ of the dimer **2** showed a potential similar to that of the monomer **8a**. Furthermore, the trimer **3** possesses three reversible redox waves at 0.03 (2e), 0.08 (1e), and 0.37 V (3e). The splitting of the first wave into two waves can be regarded as the two differently substituted TTFs with different oxidation potentials. In other words, one is the inner TTF with two thienylethyne groups, and the other is the terminal TTF with one thienylethyne group. The tetramer **4** also has three redox waves reflecting two inner TTFs and two terminal TTFs.

In summary, we have succeeded in the syntheses of thienylene-ethynylene-TTF oligomers up to hexamer via iodination with $C_6F_{13}I$, followed by the Sonogashira reactions in moderate to good yields. The electronic spectra showed partial intramolecular charge transfer between the TTF and thienylethyne units. The effective conjugation length of the oligomers is longer than the hexamer **6**. The CV of the oligomers revealed multi-redox processes owing to the two different TTF units.

EXPERIMENTAL

NMR spectra were recorded on JEOL JNM-EX 500 instrument (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). Spectra are reported (in δ) referred to internal $(CH_3)_4Si$. MS spectra were measured by JEOL JMS-AX 500 instrument. X-ray crystal analysis was measured by Rigaku AFC-7R four-circle diffractometer with graphite monochromated Mo-Kα radiation. Cyclic voltammograms were recorded on a BAS CV-27 voltammeric analyzer. Electronic absorption spectra were recorded on a Shimadzu UV-VIS-NIR scanning spectrophotometer (Model UV-3101-PC). All solvents were dried by conventional procedures and distilled before use.

4,5-Bis(butylthio)-4′,5′-bis(2-thienylethynyl)tetrathiafulvalene (1a)

To a solution of **7a** (100 mg, 0.16 mmol) and 2-ethynlthiophene (51 mg, 0.47 mmol) in Et_3N (2 mL) and benzene (3 mL), CuI (6 mg, 32 μmol) and $Pd(PPh_3)_4$ (18 mg, 16 μmol) were added, and the mixture was stirred for 4 h. Then, the mixture was filtrated through Celite, and the filtrate was poured into aq. sat. NH_4Cl solution and extracted with ether. The organic layer was washed with brine and dried over $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel with CS_2 as eluent to afford **1a** (78 mg, 82%) as an orange powder, together with **8a** (6 mg, 8%). **1a**: FAB-MS (*m*-NBA) $m/z = 593$ ($M^+ + 1$). ^{1}H NMR ($CDCl_3$): $\delta = 7.36$ (m, 2H), 7.31 (m, 2H), 7.02 (m, 2H), 2.83 (t, $J = 7.3$ Hz, 4H), 1.62 (quint, $J = 7.3$ Hz, 4H), 1.44 (sext, $J = 7.3$ Hz, 4H), 0.91 (t, $J = 7.3$ Hz, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 133.2$, 129.9, 127.8, 127.4, 121.9, 120.2, 112.5, 107.2, 92.6, 84.5, 36.1, 31.8, 21.7, 13.6.

8a: FAB-MS (*m*-NBA) $m/z = 486$ (M^+). ^{1}H NMR ($CDCl_3$): $\delta = 7.36$–7.32 (m, 4H), 7.00 (m, 2H) 6.55 (s, 1H), 2.83 (t, $J = 7.3$ Hz, 4H), 1.62 (quint, $J = 7.3$ Hz, 4H), 1.44 (sext, $J = 7.3$ Hz, 4H), 0.92 (t, $J = 7.3$ Hz, 6H).

4,5-Bis(methylthio)-4′,5′-bis(2-thienylethynyl)tetrathiafulvalene (1b)

The synthesis of **1b** was carried out in 72% yield in a similar manner as described for **1a**. **1b**: TOF-MS $m/z = 508$ (M^+). ^{1}H NMR ($CDCl_3$): $\delta = 7.37$ (m, 2H), 7.31 (m, 2H), 7.02 (m, 2H), 2.44 (s, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 133.0$, 128.8, 127.2, 121.7, 119.9, 113.8, 108.5, 92.5, 84.4, 19.29.

Synthesis of the Dimer 2

To a solution of **12** (100 mg, 0.16 mmol) and **14** (86 mg, 0.17 mmol) in Et_3N (2 mL) and benzene (10 mL), CuI (5.9 mg, 16 μmol) and $Pd(PPh_3)_4$ (18 mg, 8 μmol) were added, and the mixture was stirred for 6 h under Ar atmosphere. The mixture was poured into aq. sat. NH_4Cl solution and extracted with ether. The combined organic layer was washed with brine and dried over $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel with benzene-hexane (v/v = 1:4) as eluent to give the dimer **2** (115 mg, 72%) as an orange oil: ^{1}H NMR ($CDCl_3$) $\delta = 6.54$ (s, 2H), 2.82 (t, $J = 7.3$ Hz, 4H), 2.83 (t, $J = 7.3$ Hz, 4H), 2.59 (t, $J = 7.3$ Hz, 4H), 1.51–1.62 (m, 12H), 1.37–1.50 (m, 12H), 0.91–0.97 (m, 18H). ^{13}C NMR ($CDCl_3$) $\delta = 147.9$, 128.0, 124.5, 119.0, 115.6, 112.1, 109.7, 108.3, 87.2, 86.8, 36.0, 32.2, 31.8, 31.7, 28.2, 22.6, 21.6, 13.9, 13.6.

Synthesis of the Trimer 3

In a similar manner for the synthesis of **2**, the trimer **3** was prepared starting from **12** (203 mg, 0.33 mmol) and **7a** (82 mg, 0.13 mmol). The trimer **3** (152 mg, 72%) was obtained as a reddish oil: ^{1}H NMR ($CDCl_3$) $\delta = 6.56$ (s, 2H), 2.68–2.84 (m, 12H), 2.62 (t, $J =$ 7.3 Hz, 4H), 2.61 (t, $J = 7.3$ Hz, 4H), 1.29–1.66 (m, 20H), 1.29–1.66 (m, 20H), 0.89–0.98 (m, 30H). ^{13}C NMR ($CDCl_3$) $\delta = 148.5$, 148.1, 128.1, 127.8, 127.7, 120.0, 119.6, 119.0, 115.6, 113.0, 112.0, 109.8, 108.9**,** 92.7, 87.7, 87.5, 86.9, 36.1, 36.0, 32.2, 31.8, 28.4, 28.2, 22.6, 22.5, 21.6, 13.9, 13.9, 13.6.

Synthesis of the Tetramer 4

In a similar manner for the synthesis of **2**, the tetramer **4** was prepared starting from **12** (99 mg, 0.16 mmol) and **15** (100 mg, 0.08 mmol). The tetramer **4** (61 mg, 34%)

was obtained as a reddish oil: ^{1}H NMR ($CDCl_3$) $\delta = 6.53$ (s, 2H), 2.81–2.85 (m, 16H), 2.57–2.65 (m, 12H), 1.30–1.70 (m, 56H), 0.92–0.95 (m, 12H), 0.87–0.90 (m, 30H). ^{13}C NMR ($CDCl_3$) $\delta = 148.6$, 148.5, 148.1, 128.1, 127.9, 127.7, 124.7, 120.2, 119.9, 119.9, 119.7, 119.6, 118.9, 115.6, 113.1, 112.1, 109.7, 108.8, 92.8, 92.7, 88.1, 87.8, 87.6, 86.9, 36.1, 36.0, 32.3, 32.2, 31.8, 31.78, 28.5, 28.3, 22.63, 22.58, 21.7, 14.0, 13.6.

Synthesis of the Pentamer 5

In a similar manner for the synthesis of **2**, the pentamer **5** was prepared starting from **12** (41 mg, 65 μmol) and **13** (61 mg, 33 μmol). The pentamer **5** (58 mg, 61%) as a brown powder: LDI-TOF-MS $m/z = 2860$ (M^+). ^{1}H NMR ($CDCl_3$) $\delta = 6.53$ (s, 2H), 2.83–2.85 (m, 20H), 2.60–2.64 (m, 16H), 1.30–1.72 (m, 72H), 0.86–0.97 (m, 54H).

Synthesis of the Hexamer 6

In a similar manner for the synthesis of **2**, the trimer **3** was prepared starting from **12** (44 mg, 70 μmol) and **15** (70 mg, 28 μmol). The hexamer **6** (53 mg, 54%) as a brown powder: ^{1}H NMR ($CDCl_3$) $\delta = 6.51$ (s, 2H), 2.83–2.86 (m, 24H), 2.60–2.64 (m, 20H), 1.30–1.70 (m, 88H), 0.86–0.97 (m, 66H).

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