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Synthesis and Properties of New Trimeric and Tetrameric Tetrathiafulvalenes with Alternate Links

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Trimeric and tetrameric TTFs **1** and **2** linked alternately by methylenedithio groups were synthesized. Cyclic voltammetry and spectroelectrochemistry indicated that the dicationic state of tetrameric TTF **2** exhibited the mixed-valence state constructed not by the tetrameric TTF units but by two dimeric mutually independent TTF units.

It is well known that the strong face-to-face interaction between molecules plays a significant role in organic conductors[1,2] and one-dimensional conducting nanofibers[3] for transportation of charge carriers. Tetrathiafulvalene (TTF) and its derivatives easily form molecular assemblies thanks to the strong face-to-face interactions, and their radical cation salts with mixed-valence (MV) state often show high conductivity.[1,2] This interaction depends on the distance between the TTF units, and its distance can be easily controlled when an appropriate spacer group is used as a linker between the TTF units. Investigation of these TTF oligomers is helpful not only to understand the face-to-face interaction between the TTF units but also to construct more conductive molecular assembly.[4]

Oligomers of TTF derivatives linked by various spacers such as σ bonds, π bonds, and chalcogens have been synthesized to date.[5,6] As for linkage patterns, there are two types; one is linkage unilaterally at one-side of the TTF units and the other is linkage alternately at both sides of the TTF units (Chart 1). While TTF oligomer systems with unilateral links have been widely studied,[5] alternately linked TTF oligomers have scarcely been investigated except for directly linked TTF oligomers.[4a] Since the types of linkage in TTF oligomers give rise to diverse conformational changes in the neighboring TTFs, various intramolecular interactions depending on the linkage patterns can be anticipated. In this letter, we report synthesis and redox behavior of alternately linked trimeric and tetrameric TTFs with methylenedithio spacers, **1** and **2**. UV–vis–NIR spectroscopic characteristics of their oxidized species are also presented.

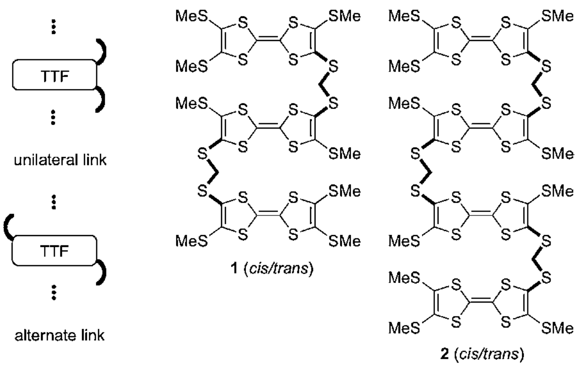
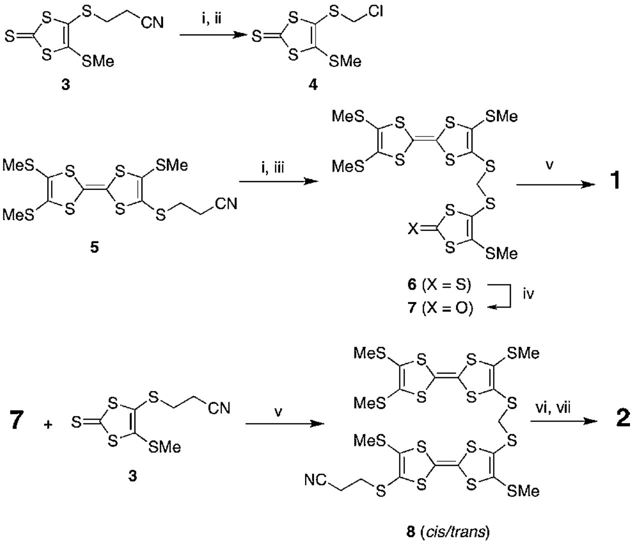


Chart 1.

The synthesis of **1** and **2** was carried out according to Scheme 1. The compound **3**[7b] was treated with one equivalent of $CsOH \cdot H_2O$ at room temperature, followed by reaction with chloroiodomethane to afford **4** in 75% yield. Treatment of **5**[7] with $CsOH \cdot H_2O$ at room temperature and subsequent reaction with **4** affords **6** in 70% yield. The thioketone **6** was converted to ketone **7** in 94% yield by reaction with mercury(II) acetate at room temperature. Triethyl phosphite-mediated self-coupling reaction of **7** provided the desired trimeric TTF **1** in 66% yield.[8] The precursor of **2** was prepared from similar cross-coupling reaction between ketone **7** and thioketone **3** in 43% yield. Dimeric TTF **8** was treated with $CsOH \cdot H_2O$, followed by reaction with diiodomethane to give the target tetrameric TTF alternately linked at both sides **2** in 64% yield.[8]

The electronic spectra measured in dichloromethane exhibited three absorption maxima at 389 (sh), 335, and 314 nm for **1**, and at 390 (sh), 336, and 315 nm for **2**. The positions of absorption maxima of both compounds were similar to the corresponding monomeric compounds **9** (398 (sh), 333, and 312 nm) and dimeric **10** (392 (sh), 333, and 310 nm) (Chart 2).[9] That is, the absorption maxima do not red-shift in spite of the increase of the TTF units, which suggested little interaction between the neutral TTF units.



Scheme 1. Reactions and conditions: (i) $CsOH \cdot H_2O$, DMF, rt, (ii) ICH_2Cl, rt, (iii) **4**, rt, (iv) $Hg(OAc)_2$, AcOH, $CHCl_3$, rt, (v) $P(OEt)_3$, toluene, 110 °C, (vi) $CsOH \cdot H_2O$, THF, rt, (vii) CH_2I_2, rt.

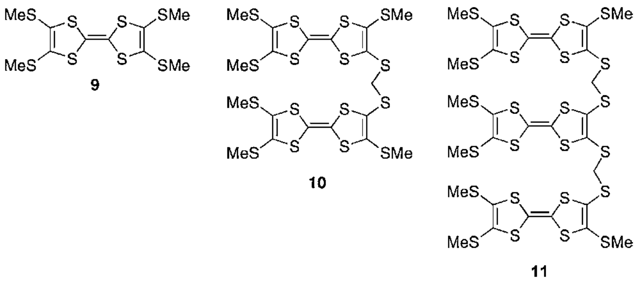


Chart 2.

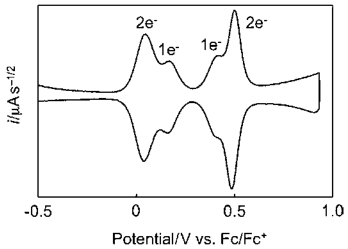


Figure 1. Deconvoluted cyclic voltammogram of **1** in benzonitrile containing 0.1 M n-Bu$_4$NPF$_6$.

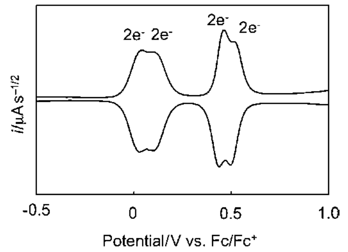


Figure 2. Deconvoluted cyclic voltammogram of **2** in in benzonitrile containing 0.1 M n-Bu$_4$NPF$_6$.

Electrochemical properties of **1** and **2** were studied by cyclic voltammetry. Figures 1 and 2 show deconvoluted voltammograms of **1** and **2** measured in benzonitrile, and their redox potentials are summarized in Table 1. The trimeric TTF **1** exhibited four pairs of redox waves at +0.04, +0.16, +0.41, and +0.49 V. Comparison of the peak currents of each wave indicated that the first and fourth oxidations involved two-electron transfer, while the second and the third waves corresponded to one-electron transfer. The splitting of the redox waves indicated mutual interactions between the TTF units in the oxidized states. Namely, the dicationic state of **1** was stabilized due to delocalization of two positive charges among the three TTF units, although the positive charges might distribute over the outer TTF units more than the central TTF unit.[9] In contrast, **1**$^{3+}$ was destabilized by a strong Coulombic repulsion among three units of (TTF)$^{\bullet+}$. Similarly to **1**$^{2+}$, **1**$^{4+}$ may be also stabilized by delocalization of four positive charges among three TTF units. The redox behavior and potentials of **1** have a close resemblance to those of a recently reported unilateral linked trimeric TTF **11**.[5a] This indicated that redox behavior does not depend on the position of linkage between the TTF units.

On the other hand, the tetrameric TTF **2** exhibited four pairs of redox waves at +0.04, +0.10, +0.45, and +0.51 V. The peak currents of all the redox waves were almost the same, which indicated all the redox processes corresponded to two-electron transfer. Fabre and co-workers reported a tetrameric TTF with unilateral propylenedithio links.[5b] In their system, the first four-electron redox process was observed as one broad four-electron redox wave and it was attributed to very small mutual interaction among the TTF units. In our tetrameric TTF system, the redox couple **2**$^{2+}$/**2** and **2**$^{4+}$/**2**$^{2+}$ can be observed as distinctly separated waves. This suggested that the interaction in **2** was stronger than that in the tetrameric TTF with unilateral propylenedithio links. The strong interaction leads to stabilization of **2**$^{2+}$. Since the redox potential of **2**$^{4+}$/**2**$^{2+}$ couple ($E_{m2} = +0.10$ V) was lower than the E_3 of **1** (+0.16 V), on-site Coulombic repulsion of **2**$^{4+}$ was smaller that of **1**$^{3+}$. Independent observation of the redox processes of **2**$^{6+}$/**2**$^{4+}$ and **2**$^{8+}$/**2**$^{6+}$ couples indicated that the tetrameric TTF with six positive charges was more stable than **2**$^{8+}$ probably due to an attractive mutual interaction among the TTF units.

Table 1. Redox potentials of **1**, **2**, and related compounds[a]

Compound	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8
	E_{m1}[b]		E_{m2}[b]		E_{m3}[b]		E_{m4}[b]	
1	+0.04		+0.16	+0.41	+0.49			
2	+0.04		+0.10		+0.45		+0.51	
9	+0.04	+0.36						
10	+0.03		+0.44					
11	+0.05		+0.17	+0.42	+0.48			

[a] In benzonitrile containing 0.1 M n-Bu$_4$NPF$_6$ at 25 °C using Pt working and counter electrodes. All potentials (V) were measured against Ag/Ag$^+$ electrode and converted to the value vs. Fc/Fc$^+$. [b] $E_{m1} = (E_1 + E_2)/2$, $E_{m2} = (E_3 + E_4)/2$, $E_{m3} = (E_5 + E_6)/2$, $E_{m4} = (E_7 + E_8)/2$.

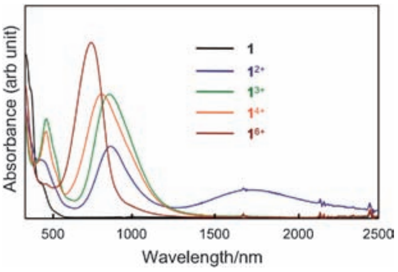


Figure 3. Electronic spectra of **1** and its oxidized species in benzonitrile.

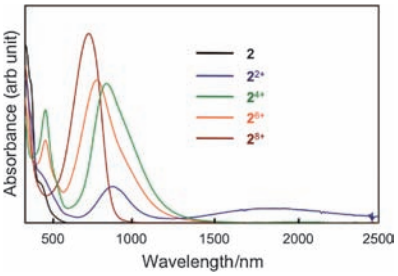


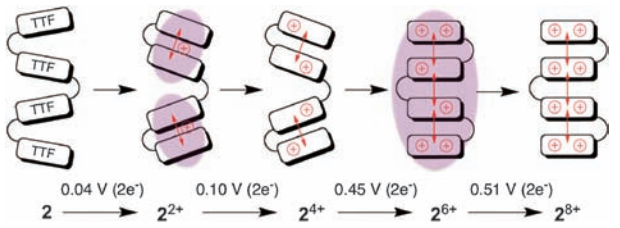
Figure 4. Electronic spectra of **2** and its oxidized species in benzonitrile.

Electrochemical oxidations of **1** and **2** were carried out in benzonitrile by applying constant voltage to produce specific oxidation states. Figures 3 and 4 show the electronic spectra of the oxidized species of **1** and **2**,[10] and their absorption maxima are summarized in Table 2. The spectrum of each oxidized state of **1** was similar to that of corresponding oxidized trimeric TTF **11**.[5a] The dication **1**$^{2+}$ exhibited two absorption maxima at 839 and

Table 2. Absorption maxima of the oxidized species of **1** and **2** in benzonitrile

Compound	Partially oxidized state I[a]	Radical cation per each TTF unit	Partially oxidized state II[b]	Dication per each TTF unit
1	839, 1712 ($\mathbf{1}^{2+}$)	430, 824 ($\mathbf{1}^{3+}$)	430, 774 ($\mathbf{1}^{4+}$)	709 ($\mathbf{1}^{6+}$)
2	851, 1903 ($\mathbf{2}^{2+}$)	427, 825 ($\mathbf{2}^{4+}$)	427, 776 ($\mathbf{2}^{6+}$)	710 ($\mathbf{2}^{8+}$)
11	436, 850, 1756 ($\mathbf{11}^{2+}$)	436, 840 ($\mathbf{11}^{3+}$)	436, 780, 963 (sh) ($\mathbf{11}^{4+}$)	731 ($\mathbf{11}^{6+}$)
10	850, 1880 ($\mathbf{10}^{\bullet+}$)	432, 837 ($\mathbf{10}^{2+}$)		725 ($\mathbf{10}^{4+}$)
9		473, 884 ($\mathbf{9}^{\bullet+}$)		737 ($\mathbf{9}^{2+}$)

[a]Partially oxidized state between neutral and monocation per TTF unit. [b]Partially oxidized state between monocation and dication per TTF unit.



Scheme 2. Plausible redox scheme of **2**.

1712 nm. The absorption maximum at 1712 nm was assigned to the MV band derived from the SOMO–HOMO transition.[11] The trication $\mathbf{1}^{3+}$ exhibited two absorption maxima at 430 and 824 nm, and the MV band was not observed. Absorption maxima of $\mathbf{1}^{2+}$ and $\mathbf{1}^{3+}$ were blue-shifted compared with $\mathbf{9}^{\bullet+}$ (473 and 884 nm). This blue-shift is known as the Davydov blue-shift, which is due to the π–π interaction between the cation radicals.[12] Similar blue shifts were also observed in $\mathbf{1}^{4+}$ and $\mathbf{1}^{6+}$. Because of this observation of Davydov blue-shift, three cationic TTF units are thought to form a face-to-face stack to bring the interaction among them. This interaction acts to stabilize the $\mathbf{1}^{4+}$ state.

The dication of the tetramer $\mathbf{2}^{2+}$ gave absorption maxima at 851 and 1903 nm. The broad band centered at 1903 nm was attributed to the MV state. The wavelength of the MV band was closer to that of $\mathbf{10}^{\bullet+}$ (1880 nm) compared to $\mathbf{1}^{2+}$ (1712 nm).[5a] Furthermore, the redox process between $\mathbf{2}^{2+}$ and $\mathbf{2}^{4+}$ was observed as simultaneous two-electron redox waves. These results suggested that the MV state in $\mathbf{2}^{2+}$ was not constructed by four whole TTF units, but by two independently interacting two-TTF units as shown in Scheme 2. The absorption maxima at 427 and 825 nm in $\mathbf{2}^{4+}$ and 427 and 776 nm in $\mathbf{2}^{6+}$ were Davydov blue-shifted compared with those of $\mathbf{9}^{\bullet+}$ (473 and 884 nm),[12] indicating a π–π interaction in $\mathbf{2}^{4+}$ and $\mathbf{2}^{6+}$. Although there is π–π interaction in the $\mathbf{2}^{4+}$ state, the most plausible structure of the $\mathbf{2}^{4+}$ state is also constructed of independently interacting two TTF units, because E_{m2} of **2** is lower than E_3 of **1** where all three TTF units are responsible for the oxidation. Considering such a significant blue shift in the electronic spectra together with the E_{m2} of **2** being lower than the E_3 of **1**, we assume the most plausible structure of the $\mathbf{2}^{4+}$ state is also constructed of two independently interacting TTF units. Absorption maxima of $\mathbf{2}^{6+}$ and $\mathbf{2}^{8+}$ also showed the Davydov blue-shift, which indicated the π–π interaction between the TTF units. Probably, hexacationic and octacationic states have a stacking form.

In summary, we demonstrated the synthesis and properties of trimeric and tetrameric TTF oligomers with alternate links. The linkage patterns of the present oligomers led to novel interactions in the oxidation stages. Further investigation, especially, preparation of higher TTF oligomers with alternate and unilateral links as well as more detailed investigations on the redox behavior of **1** and **2** are actively in progress.

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8 **1**: 66% yield; orange solid; mp 53–55 °C; IR (KBr): ν 2963, 2854, 1416, 1309, 1262, 1020, 883 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$): δ 4.17–4.15 (4H, s), 2.47–2.45 (4H, m), 2.43–2.42 (4H, m); ^{13}C NMR (100 MHz, CDCl$_3$): δ 19.19, 19.26, 19.35, 19.41, 19.43, 42.56, 110.32, 110.36, 110.76, 110.79, 111.31, 111.38, 122.29, 122.40, 122.42, 122.45, 127.41, 127.44, 127.51, 133.79, 133.83, 133.87, 133.95; MS (LDI) *m*/*z*: M$^+$ 1132. **2**: 64% yield; yellow solid; mp 65–67 °C; IR (KBr): ν 2914, 1483, 1419, 1386, 1310, 1120, 965, 890, 817 cm^{-1}; ^{1}H NMR (270 MHz, CDCl$_3$): δ 4.17–4.16 (6H, m), 2.47–2.46 (18H, m), 2.43–2.42 (12H, m); ^{13}C NMR (100 MHz, CDCl$_3$): δ 19.22, 19.23, 19.26, 19.28, 19.31, 19.33, 19.40, 19.42, 19.44, 19.45, 19.47, 19.48, 22.66, 31.59, 42.87, 109.57, 110.15, 111.62, 112.06, 121.93, 127.41, 127.46, 127.57, 127.62, 128.83, 129.46, 134.25; MS (LDI) *m*/*z*: M$^+$ 1504. The *cis*/*trans* mixture of **1** and **2** were usually obtained and they were hardly separated. Cyclic voltammetric and spectroscopic experiments were carried out by using the *cis*/*trans* mixture.

9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

10 As for the trimer **1**, the voltages at 0.10, 0.35, 0.45, and 0.65 V (E_{pc} values, vs. Fc/Fc$^+$) corresponding to the formation of $\mathbf{1}^{2+}$, $\mathbf{1}^{3+}$, $\mathbf{1}^{4+}$, and $\mathbf{1}^{6+}$ were adopted based on the results of CV. In case of $\mathbf{1}^{2+}$, the cathodic peak top of the first oxidation wave was applied. Similarly, the voltages at 0.05, 0.40, 0.6, and 1.0 V (E_{pc} values, vs. Fc/Fc$^+$), corresponding to the formation of $\mathbf{2}^{2+}$, $\mathbf{2}^{4+}$, $\mathbf{2}^{6+}$, and $\mathbf{2}^{8+}$, were applied.

11 The MV absorption was observed even in diluted solution, the absorption was resulted from intramolecular interaction of the folded $\mathbf{1}^{2+}$ in solution.

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