

Dimeric and Trimeric Tetrathiafulvalenes with Strong Intramolecular Interactions in the Oxidized States

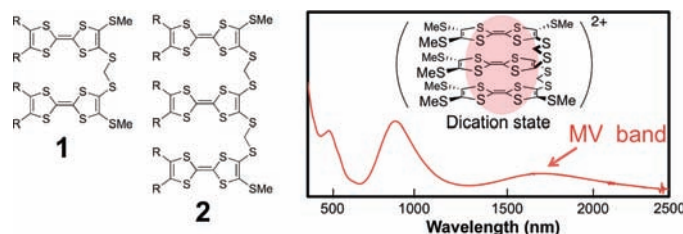
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ABSTRACT



New dimeric and trimeric TTF derivatives with methylenedithio spacers (1a,b, 2a, and 2b) have been synthesized. X-ray structure analysis revealed that TTF units of the dimer 1b adopted distorted face-to-face overlapping arrangement both in intra- and intermolecular stacking. Cyclic voltammetric study indicated that trimeric 2a was in favor of taking di- and tetracationic states, while the dimeric 1a was in favor of taking a monocation. The absorption spectroscopic study suggested an existence of the strong face-to-face interaction particularly in di-, tri-, and tetracationic state of the trimeric TTF derivatives.

Molecular conductors^{1,2} and 1D-nanofibers³ often consist of a molecular assembly that has strong face-to-face interactions. In particular, tetrathiafulvalene (TTF) and its derivatives have received considerable attention as donor (D) components of the molecular assembly because they have strong electron-donating ability as well as high planarity in the oxidized state.^{1,2} The donor component molecules in the conducting materials form face-to-face molecular stacks with partially oxidized state. Thus, investigations of the face-to-face interaction in donor

molecules is inevitable to construct efficient molecular conductors.⁴

A number of TTF dimers with various spacers have been synthesized so far.^{4–6} In most dimeric TTF systems, a mixed

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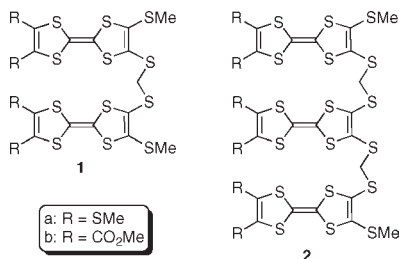
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valence (MV) state of TTF (namely (TTF)⁻(TTF^{•+}) is stabilized by intramolecular CT interaction, while (TTF^{•+})⁻(TTF^{•+}) is energetically unstable because of the strong Coulombic repulsion.^{7,8} As a result, the redox wave in the cyclic voltammogram corresponding to the first two-electron oxidation often splits into two pairs of one-electron redox waves. Stacked TTF trimeric or higher oligomeric systems were scarcely studied electrochemically to elucidate their electronic structures.⁹ Fabre and Carcel reported synthesis and redox properties of trimeric TTF oligomers with a propylenedithio spacer (-SCH₂CH₂CH₂S-).^{9a} In their system, the dimeric MV state, not the trimeric MV state, was responsible for the formation of one-electron oxidized radical cation.

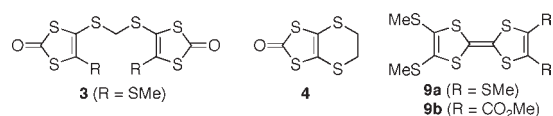
Study of redox properties combined with absorption spectroscopy in the TTF-stacked system with another spacer group will give further insight into understanding the interaction between the TTF units. In this paper, we report synthesis, structures, electrochemical properties, and absorption spectra of new dimeric and trimeric TTF derivatives with methylenedithio spacers **1** and **2** and discuss the face-to-face interaction between the TTF units.



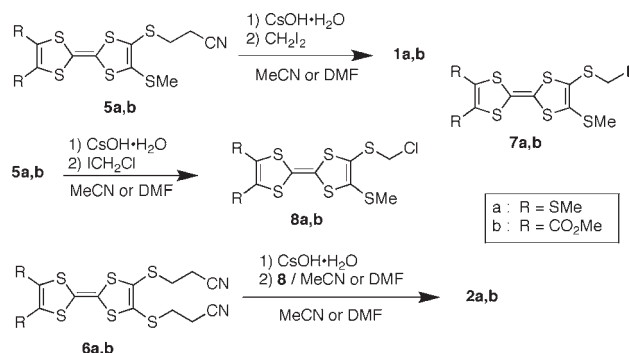
Sugawara and co-workers reported the synthesis of **1** (R = SCH₂CH₂S) by phosphite-mediated cross-coupling between **3** and **4**.^{5c} This methodology has a disadvantage; separation of the desired product from the homocoupling products is usually difficult. In particular, the homocoupling reaction of the diketone **3** might afford many oligomeric (and/or polymeric) products. Thus, a different methodology is desired. We adopted TTF derivatives with a 2-cyanoethylthio group **5a,b**¹⁰ as starting materials. The compounds **5a,b** were prepared from 4,5-bis(2-cyanoethylthio)-TTF derivatives **6a,b**,^{10b} which can be easily separated from the homocoupling products. As shown in Scheme 1, **5a,b** were treated with CsOH·H₂O at room temperature. The resultant TTF-thiolates were

allowed to react with an excess of diiodomethane to give dimeric TTF derivatives **1a,b** in 83 and 80% yields, respectively. In this reaction, the monoadducts **7a,b** were not obtained at all. This result can be explained by higher reactivity of **7** with TTF-thiolate compared with diiodomethane, considering the high reactivity of α -halo(thio)ether. In contrast, a similar reaction was carried out by use of chloriodomethane to give the corresponding monoadducts **8a,b** in 63 and 92% yields, respectively. Treatment of **6a,b** with 2 molar equiv of CsOH·H₂O at rt, followed by the reaction with 2 molar equiv of **8a,b**, afforded the target trimeric TTFs (**2a,b**) in 46% and 56% yields, respectively.

Electronic spectra of **1a**, **2a**, and the corresponding monomeric compound **9a** exhibited similar absorption maxima at ca. 398, 333, and 312 nm.¹¹ No distinct redshift was observed as the number of TTF units increased, while molecular absorption coefficients became larger as the number of TTF units increased. This result indicates that there is little interaction between TTF units in the neutral state.



Scheme 1



Single crystals of **1b** were obtained from the THF solution as purple plates by slow evaporation of the solvent at rt, and X-ray structure analysis was performed.¹² The compound **1b** crystallized in the orthorhombic system, space group $P2_12_12_1$. The molecular structure is shown in Figure 1. Two TTF units in the compound **1b** are overlapping with a slightly off-aligned face-to-face arrangement, although the spacer bridge chain, the methylenedithio group, is flexible enough to allow the molecule to have a complete overlapping configuration. This could be due to a compromise between the π - π interaction of the TTF units which is in favor of having overlapping configuration and the steric hindrance derived from thiomethyl and

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(11) See the Supporting Information.

(12) Crystal data for **1b**: C₂₃H₂₀O₈S₁₂, FW = 809.13, purple plate, orthorhombic, $P2_12_12_1$, $a = 7.698(2)$ Å, $b = 15.339(3)$ Å, $c = 28.236(7)$ Å, $V = 3334.0(14)$ Å³, $\mu = 0.830$ mm⁻¹, $Z = 4$, 36886 reflections measured, 7584 unique ($R_{int} = 0.1503$). Final R indices [$I > 2\sigma(I)$]: $R1 = 0.0777$, $wR2 = 0.1760$, GOF = 0.788.

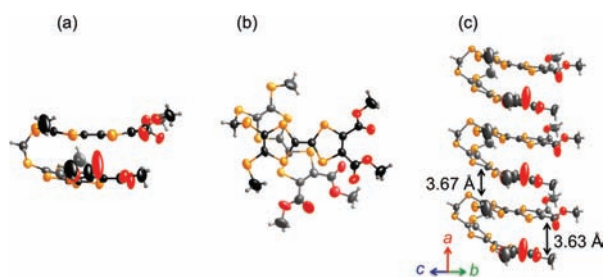


Figure 1. X-ray structure of **1b**: (a) side view, (b) top view, and (c) stacking structure.

methoxycarbonyl groups. This structure is quite different from the previously reported cationic TTF dimer bridged with the same methylenedithio spacer, which took a completely overlapping configuration.^{5c} The compound **1b** in the neutral state seems to have a rather weak face-to-face interaction. Each TTF moiety has a tub conformation with a folded angle of 7.8° . The intraplanar distance between the TTF mean planes is 3.63 \AA . The molecules form a uniform column along the *a* axis. The interplanar distance between the mean TTF planes of the neighboring molecules is 3.67 \AA . It is remarkable that the intra- and interplanar distances are very close.

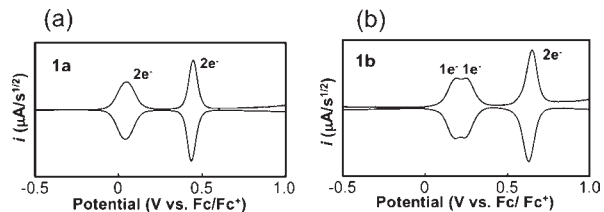


Figure 2. Deconvoluted cyclic voltammograms of (a) **1a** and (b) **1b** in benzonitrile containing $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$.

Electrochemical properties of **1** and **2** were investigated by cyclic voltammetry. Figure 2 shows deconvoluted voltammograms of **1a** and **1b** measured in benzonitrile solution. The compound **1a** exhibited two pairs of redox waves at 0.03 and 0.44 V , both of which corresponded to two-electron transfer (Table 1). The first redox wave was broadened because of a mutual interaction between the two TTF units in $\mathbf{1a}^{+\bullet}$ and/or $\mathbf{1a}^{2+}$. In contrast, the first two-electron redox process of **1b** split into two redox waves, and three totally reversible redox waves were observed at 0.17 , 0.24 , and 0.64 V , respectively. Comparison of peak currents of each wave indicates that the first and second oxidations afforded $\mathbf{1b}^{+\bullet}$ and $\mathbf{1b}^{2+}$ and the third oxidation gave $\mathbf{1b}^{4+}$, respectively. Such splitting or broadening of the first wave suggests mutual interaction between two TTF units with the states of $\mathbf{1}^{+\bullet}$ and $\mathbf{1}^{2+}$ as has been observed in many TTF dimers.⁴ Namely, $\mathbf{1}^{+\bullet}$ is stabilized by delocalization of a positive charge on the two TTF units, while $\mathbf{1}^{2+}$ is destabilized by

Table 1. Redox Potential^a of **1** and **2**

	$E_1^{1/2}$	$E_2^{1/2}$	$E_3^{1/2}$	$E_4^{1/2}$	$E_5^{1/2}$	$E_6^{1/2}$
1a		0.03		0.44		
1b	0.17	0.24		0.64		
2a		0.05	0.17	0.42		0.48
2b		0.21	0.30		0.63	
9a	0.04	0.36				
9b	0.19	0.53				

^a Conditions: $^n\text{Bu}_4\text{N}^+\cdot\text{PF}_6^-$ (0.1 M), benzonitrile, 25°C , Pt working and counter electrodes. Potentials were measured against Ag/Ag^+ electrode and converted to the value vs Fc/Fc^+ .

Coulomb repulsion between two $\text{TTF}^{+\bullet}$ units.^{5,6} As a result, $\mathbf{1}^{+\bullet}$ and $\mathbf{1}^{2+}$ have different redox potentials.

Deconvoluted voltammograms of the trimers **2a** and **2b** are shown in Figure 3. Cyclic voltammogram of **2a** consisted of four pairs of reversible redox waves at 0.05 , 0.17 , 0.42 , and 0.48 V (Table 1). The redox process between **2a** and $\mathbf{2a}^{3+}$ was observed as two pairs of redox waves, which correspond to two- and one-electron oxidation, respectively. This behavior is different from the TTF trimer with propylenedithio linker.⁹ Two positive charges of $\mathbf{2a}^{2+}$ probably distribute mainly on the outer TTF units so that on-site Coulombic repulsion is reduced. Furthermore, the redox process between $\mathbf{2a}^{3+}$ and $\mathbf{2a}^{6+}$ was also observed as two redox waves. In this case, the redox couple $\mathbf{2a}^{3+}/\mathbf{2a}^{4+}$ was independently observed as a one-electron transfer process, while $\mathbf{2a}^{4+}/\mathbf{2a}^{6+}$ was observed as a simultaneous two-electron transfer process. This indicates the presence of mutual interaction among the TTF units in the tetracationic state. On the other hand, the cyclic voltammogram of **2b** showed three reversible redox waves at 0.21 , 0.30 , and 0.63 V , respectively. The redox wave of $\mathbf{2b}^{3+}/\mathbf{2b}^{6+}$ was found as a broad wave, which seemed to be an almost simultaneous three-electron transfer process.

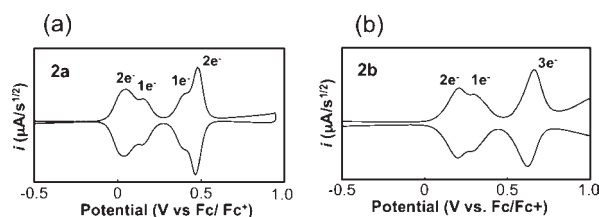


Figure 3. Deconvoluted cyclic voltammograms of (a) **2a** and (b) **2b** in benzonitrile containing $0.1 \text{ M } ^n\text{Bu}_4\text{NPF}_6$.

As can be seen in cyclic voltammograms, strong intramolecular interactions are anticipated among the TTF units at various oxidation states. We attempted spectroelectrochemistry of **1a** and **2a** together with **9a** to elucidate the details of their redox processes and their interactions. Figures 4 and 5 show the electronic spectra of **1a** and **2a** in each oxidized state generated by applying constant voltages.¹³ The cation radical

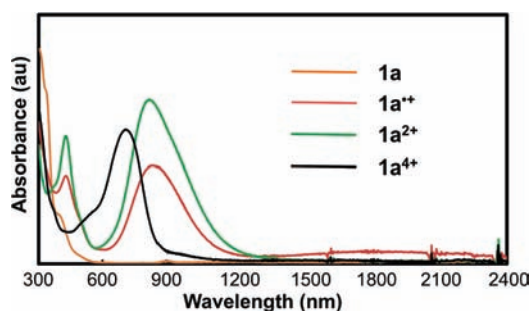


Figure 4. Electronic spectra of **1a** and its oxidative species.

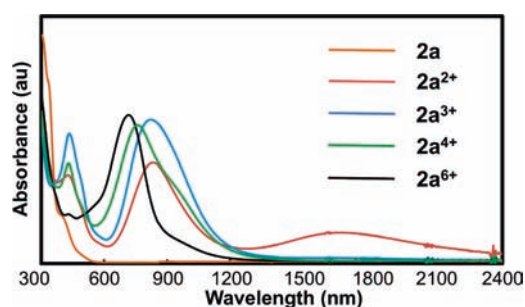


Figure 5. Electronic spectra of **2a** and its oxidative species.

1a⁺ exhibited three absorption maxima at 436, 850, and 1880 nm. The absorption maximum at 1880 nm was assigned to be a mixed-valence (MV) band derived from the SOMO–HOMO transition between the stacked (TTF)–(TTF⁺) units.¹⁴ The MV band disappeared in the dication state. Furthermore, absorption maxima of 432 and 837 nm were blueshifted compared with corresponding peaks in **9a**⁺. These spectral features were attributed to the π – π interaction known as the Davydov blueshift¹⁵ in the cation-radical π -dimer. The absorption spectrum of **1a**⁴⁺ did not show the absorption band at a longer wavelength region ($\lambda > 1350$ nm), which was an indication of the absence of the MV state.

The trimer **2a**²⁺ gave a spectrum similar to the dimer **1a**⁺, and its absorption maxima were observed at 436, 850, and 1756 nm. The absorption maximum at 1756 nm was

(13) As for the dimer **1a**, the voltages at 0.05, 0.30, and 0.8 V (E_{pc} values, vs Fc/Fc⁺) corresponding to the formation of **1a**⁺, **1a**²⁺, and **1a**⁴⁺ were employed on the basis of the results of CV. In the case of **1a**⁺, the cathodic peak top of the first oxidation wave was applied. Similarly, the voltages at 0.10, 0.50, 0.8, and 1.0 V (E_{pc} values vs Fc/Fc⁺), corresponding to the formation of **2a**²⁺, **2a**³⁺, **2a**⁴⁺, and **2a**⁶⁺, were applied.

(14) The MV absorption was observed even in diluted solution; the absorption resulted from intramolecular interaction of the folded **1a**⁺ in solution.

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assigned to be the MV band attributed to significant face-to-face interactions in **2a**²⁺.¹⁴ The MV band probably results from delocalization of two positive charges among the three TTF units as shown in Figure 6. However, resonance structure B should be the most contributing so as to avoid Coulombic repulsion. The spectrum of **2a**³⁺ showed two absorption maxima at 840 and 436 nm with no MV band. These maxima were Davydov blueshifted compared with corresponding maxima in **9a**⁺, which was the result of the contribution of the stacked cation radicals in a trimer.^{7,15} The 780 nm absorption maximum in the spectrum of **2a**⁴⁺ appeared with a significant blueshift compared with the corresponding one in **9a**⁺. This peak was accompanied by a shoulder at ca. 963 nm. It should be noted that no absorption band assigned to the framework of the TTF²⁺ unit of **9a**²⁺ was observed. These features may indicate a strong intramolecular interaction among three TTF units in **2a**⁴⁺. The spectrum of fully oxidized **2a**⁶⁺ is similar to that of **1a**⁴⁺.

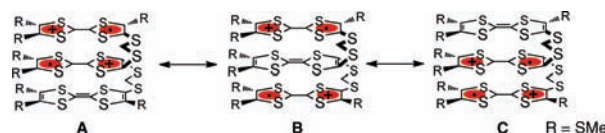


Figure 6. Plausible resonance structures of **2a**²⁺.

In summary, we have synthesized new dimeric and trimeric TTF derivatives with methylenedithio spacers. X-ray crystal analysis of neutral **1b** revealed that two TTF units adopted a slightly off aligned overlapping arrangement both intra- and intermolecularly in the stacking column. Cyclic voltammogram of **1a** consisted of one broad and one sharp redox waves, whereas that of **2a** consisted of four redox waves. Their electronic structures were studied electrochemically, and the mixed valenced band appeared in the cation radical state of **1a**. The electronic spectra of **2a** in the dication state indicated that two positive charges were delocalized in trimeric TTF, and more charges were distributed on the outer TTF units than on the sandwiched TTF unit.

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Supporting Information Available. Detailed experimental procedures and spectra of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.