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Synthesis and Properties of 1,3-Dithiole[5]dendralenes with Two Thiophene Spacers

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Novel 1,3-dithiole[5]dendralene derivatives with two thiophene spacers **3a** and **3b** were synthesized. Cyclic voltammetry and spectroelectrochemistry revealed that the positive charges of **3** in the dication and tetracation states mainly distribute on the outer two extended TTF moieties.

Extended tetrathiafulvalene (TTF) systems have received much attention as organic electronic materials represented as molecular conductors.[1] Among the various extended TTF systems synthesized so far, [*n*]dendralenes with 1,3-dithiol-2-ylidene (DT) units are of significant interest. Thus, high conductivity is expected, because on-site Coulomb repulsion in the dication may be reduced by the delocalization of two positive charges over three (or more) redox-active DT units. Furthermore, X-ray structure analysis of a derivative of [3]dendralene revealed that it has a nonplanar structure with the terminal DT unit almost orthogonally distorted, whereas the remaining vinylogous TTF moiety has high planarity.[2] Such unique nonplanar molecular structure brings expectation of a new type of multidimensional molecular packing. Several 1,3-dithiole[*n*]dendralenes ($n = 3$ and 4) have been synthesized, but the higher homologs of 1,3-dithiole[*n*]dendralenes ($n \geq 5$) are still unknown targets.[2–4] On the other hand, extended 1,3-dithiole[3]dendralene systems **1** and **2** (Chart 1) designed by insertion of a thiophene spacer were also investigated as promising molecular systems for soliton valves as well as novel redox systems.[5,6] In this letter, we report the synthesis and properties of 1,3-dithiole[5]dendralenes containing two thiophene spacer units **3a** and **3b**.

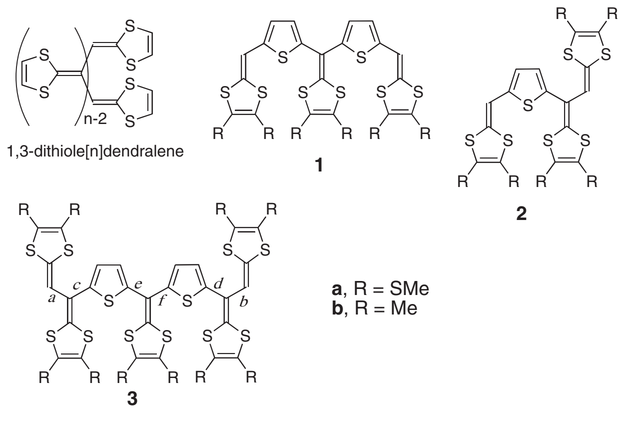
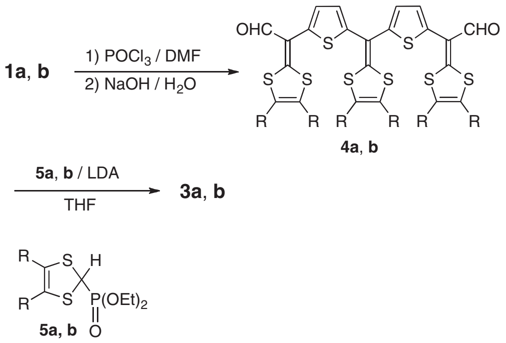


Chart 1.



Scheme 1.

The synthesis of **3a** and **3b** was achieved according to Scheme 1. The Vilsmeier–Haack reaction of **1a** and **1b** with DMF in the presence of an excess of phosphoryl chloride, followed by treatment with aqueous sodium hydroxide gave bisformylated derivatives **4a** and **4b** in 85 and 82% yields, respectively. The target molecules **3a** and **3b** were obtained in the respective yields of 87 and 43% by treatment of **4a** and **4b** with phosphonate esters **5a** and **5b** in the presence of LDA at −78 °C.[7] The new donors **3a** and **3b** were obtained as stable yellow or orange solid.

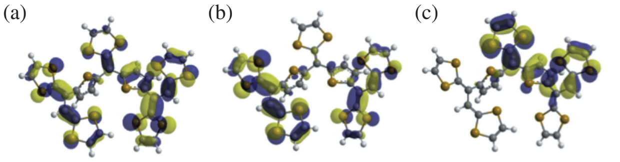


Figure 1. (a) HOMO, (b) HOMO−1, and (c) HOMO−2 of unsubstituted **3**. The energy levels are −4.35, −4.38, and −4.89 eV, respectively.

The molecular orbital calculations of unsubstituted **3** were carried out using B3LYP/6-31G(d).[8] Figure 1 shows the optimized geometry of unsubstituted **3** with the highest occupied molecular orbital (HOMO), the HOMO−1, and HOMO−2. The molecule adopts a nonplanar structure. The outer vinylogous TTF units adopt moderate planarity, and the torsion angles around the bonds *a* and *b* (Chart 1) are 27.9 and 32.0°, respectively. In contrast, the vinylogous TTF part and the neighboring thiophene ring are more distorted; the torsion angles around the bonds *c* and *d* are 57.0 and 49.3°, respectively. On the other hand, the central 1,3-dithiole ring and the thiophene ring are almost planar (22.3°), while the torsion angle around the bond between the central 1,3-dithiole ring and the other thiophene is very large (81.1°). The HOMO distributes on the whole molecule. On the other hand, the HOMO−1 mainly distributes on the outer vinylogous TTF moieties, while the HOMO−2 mainly localizes on the central dithiole ring, one of thioplene ring and on one dithiole ring in the outer vinylogous

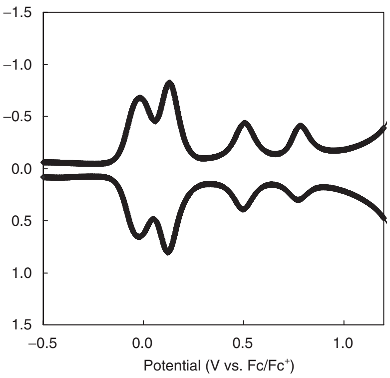
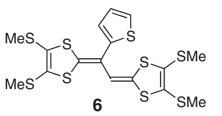


Figure 2. Deconvoluted cyclic voltammogram of **3a** in benzonitrile.

Table 1. Redox potentials of **3** and related compounds[a]

Compound	E_1	E_2	E_3	E_4	E_5	E_6
	E_{m1}[b]		E_{m2}[c]			
3a	−0.02		0.12		0.50	0.78
3b	−0.21		0.01		0.47	0.83
1a	0.04		0.35			
2a	−0.03	0.09	0.42			
6	−0.04	0.11				
7	−0.01	0.09				

[a] In PhCN containing 0.1 M Bu_4NPF_6, all potentials measured against Ag/Ag^+ reference electrode and converted to vs. Fc/Fc^+. [b] $E_{m1} = (E_1 + E_2)/2$. [c] $E_{m2} = (E_3 + E_4)/2$.



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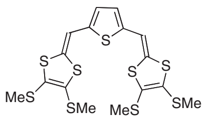

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TTF moiety. The energy levels of the HOMO (−4.35 eV) and HOMO−1 (−4.38 eV) are very close to each other, indicating the biradical character contributes to the dicationic state.

The electrochemical properties of **3** were investigated by cyclic voltammetry. Figure 2 shows the deconvoluted cyclic voltammogram of **3a** measured in benzonitrile, and their redox potentials are summarized in Table 1 together with related compounds.[9] Both the [5]dendralenes **3a** and **3b** exhibited four pairs of reversible redox waves. The peak currents of the first two redox waves are about twice as large as those of the remaining waves. Therefore, the first two waves are assigned to two-electron transfer, while the latter ones correspond to one-electron transfer. Comparing the redox potentials of **3a** with the related compounds, five positive charges are located on each of the five DT units in $\mathbf{3a}^{5+\bullet}$. The observation of the redox wave at 0.78–0.83 V may be attributed to the formation of a dithienylmethyl cation that can be stabilized by effective conjugation with two thiophene rings (Figure 3). Considering that the first two redox stages correspond to two-electron transfer and that the E_{m2} value is considerably lower than E_3 of **1a** and **2a**, dimeric extended TTF structures **3I** or **3II** should significantly contribute to the dication and tetracation states (Figure 4).

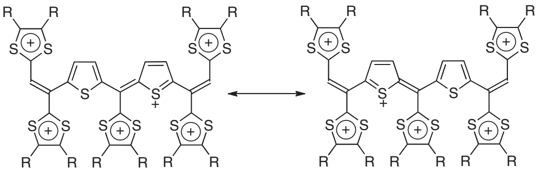
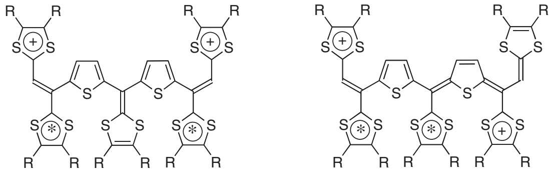


Figure 3. Plausible resonance structures of $\mathbf{3}^{6+}$.



$\mathbf{3I}^{m+}$ $\mathbf{3II}^{m+}$

Figure 4. Plausible resonance structures **3I** and **3II** of $\mathbf{3}^{m+}$: $* = \bullet$, $m = 2$; $* = +$, $m = 4$.

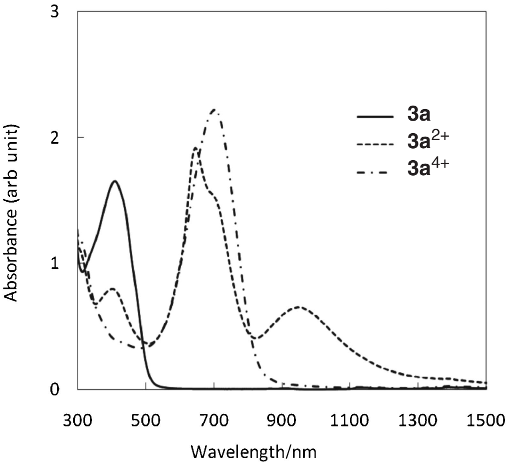


Figure 5. UV–vis–NIR spectra of **3a** (solid line), $\mathbf{3a}^{2+}$ (broken line), and $\mathbf{3a}^{4+}$ (dash-dotted line) in benzonitrile.

The oxidized species of **3a** were generated by electrochemical oxidation in benzonitrile containing Bu_4NPF_6. UV–vis–NIR spectra of $\mathbf{3a}^{2+}$ and $\mathbf{3a}^{4+}$ are shown in Figure 5 together with that of **3a**.[10] The electronic spectrum of $\mathbf{3a}^{2+}$ shows absorption maxima at 400, 645, 715, and 948 nm. On the other hand, $\mathbf{3a}^{4+}$ shows an absorption maximum at 702 nm.[10] The spectrum of $\mathbf{3a}^{2+}$ has remarkable resemblance to $\mathbf{6}^{+\bullet}$ ($\lambda_{max} = 642$, 670, and 962 nm), but is quite different from that of $\mathbf{7}^{+\bullet}$ ($\lambda_{max} = 729$ and 1201 nm).[11] These results strongly indicate that two positive charges of $\mathbf{3a}^{2+}$ mainly distribute on the outer vinylogous TTF moieties. Namely, the resonance structure $\mathbf{3I}^{2+}$ significantly contributes to the ground state of $\mathbf{3}^{2+}$, while the contribution of $\mathbf{3II}^{2+}$ is negligible. Similarly, the absorption maximum of $\mathbf{3a}^{4+}$ has greater resemblance to $\mathbf{6}^{2+}$ ($\lambda_{max} = 716$ nm) compared with $\mathbf{7}^{2+}$ ($\lambda_{max} = 772$ nm), suggesting that $\mathbf{3a}^{4+}$ can be regarded as a dimeric vinylogous TTF with a dithienylmethylidene spacer.

The further investigations, in particular, preparation of single crystals of molecular conductors based on **3** and synthesis of the related [*n*]dendralenes are actively in progress.

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7 **3a**: 87% yield; yellow powder; mp 100–103 °C; IR (KBr): 2983, 2915, 1654, 1480, 1425 cm^{-1}; ^{1}H NMR (CS_2–C_6D_6): δ 6.799 (2H, s), 6.797 (2H, s), 5.83 (2H, s), 2.34 (6H, s), 2.33 (6H, s), 2.28 (12H, s), 2.20 (6H, s); MS (m/z): 1192 (M^+); Anal. Calcd for $C_{38}H_{36}S_{22}$: C, 38.09; H, 3.03%. Found: C, 38.64; H, 3.18%. **3b**: 43% yield; orange powder; mp 150–153 °C; IR (KBr): 2911, 2850, 1628, 1488, 1437 cm^{-1}; ^{1}H NMR (CS_2–C_6D_6): δ 6.72 (2H, d, $J = 3.8$ Hz), 6.69 (2H, d, $J = 3.8$ Hz), 5.72 (2H, s), 1.92 (6H, s), 1.90 (6H, s), 1.87 (6H, s), 1.81 (6H, s), 1.75 (6H, s); MS (m/z): 872 (M^+); Anal. Calcd for $C_{38}H_{36}S_{12}$: C, 52.01; H, 4.14%. Found: C, 52.09; H, 4.76%.

8 The molecular orbital calculation was carried out using the Gaussian 03 program. M. J. Frish et al., *Gaussian 03*, Gaussian, Inc., Pittsburgh, PA, **2003**.

9 Compounds **6** and **7** were prepared according to the literatures: K. Takahashi, T. Nihira, M. Yoshifuji, K. Tomitani, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2330; T. Sugimoto, H. Awaji, I. Sugimoto, Y. Misaki, T. Kawase, S. Yoneda, Z. Yoshida, T. Kobayashi, H. Anzai, *Chem. Mater.* **1989**, *1*, 535.

10 The oxidized species **3a**$^{2+}$ and **3a**$^{4+}$ are stable enough for satisfactory measurement of UV–vis–NIR spectra. Thus, more than 90% of **3a** was recovered by the electrochemical reduction of **3a**$^{2+}$ and **3a**$^{4+}$ after the measurement of UV–vis–NIR spectra.

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