

Synthesis and Properties of 1,3-Dithiole[4]dendralenes, in Which Two Thiophene Rings Are Inserted

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Novel 1,3-dithiole[4]dendralene derivatives **3** with two thiophene spacers were synthesized. Cyclic voltammetry and spectroelectrochemistry suggested the dications of most derivatives of **3** have dimeric thiophene–quinoid radical cation structures, while tetramethyltetrakis(methoxycarbonyl) derivative **3Bd** adopts a vinylogous TTF dication structure.

Tetrathiafulvalene (TTF) and its derivatives have attracted much attention as conductive components of molecular conductors, because they have strong electron-donating properties attributed to formation of stable aromatic 1,3-dithiole rings by one- and two-electron oxidation. In the past three decades, various π -extended TTF systems have been synthesized toward realization of metallic conductivity by reducing on-site Coulomb repulsion in the dicationic state.¹ [*n*]Dendralenes with multiple 1,3-dithiole rings are expected to adopt novel molecular arrangement as well as unique multistage redox behavior, because they have several conjugated units that are not conjugated with each other due to their nonplanar structure.^{2–4} We have recently reported the synthesis of [3]- and [5]dendralenes **1** and **2** in which one or two thiophene rings were inserted (Chart 1).^{5,6} Spectroelectrochemical experiments revealed that two positive charges distribute mainly on the outer extended TTF moieties in 2^{2+} and the molecule might not take a thiophene–quinoid structure.⁶ However, 1^{2+} might take a thiophene–quinoid structure with high probability.⁵ In this connection, 1,3-dithiole[4]dendralene **3** with inserted thiophene is of interest as a multistage redox system. For example, the dication of **3** can adopt two plausible structures, namely dimeric thiophene–quinoid radical cation (Type I) and vinylogous TTF dication (Type II) as shown in Figure 1. In this letter, we report the synthesis and electrochemical properties of derivatives of **3**.

The synthesis of **3** was carried out according to Scheme 1. The oxidation of the derivatives of 6-(2-thienyl)-1,4-dithiafulvene **4A–4C** by (*p*-BrC₆H₄)₃N·SbCl₆ in dichloromethane, followed by the reduction with Zn powder in acetonitrile gave the corresponding oxidative coupling products **5A–5C** in 80–87% yields.⁷ However, the similar reaction of **4D** did not proceed, which could be due to the presence of electron-withdrawing methoxycarbonyl groups. The Vilsmeier–Haack formylation of **5A–5C** was carried out by treatment with POCl₃ in DMF at room temperature, and the bis(formyl) derivatives **6A–6C** were obtained in 85–93% yields. The Wittig or Horner–Wadsworth–Emmons reaction of **6A–6C** with the corresponding organophosphorus reagent **7** or **8** in the presence of LDA gave the target [4]dendralenes **3** in 22–84% yields.⁸

Molecular orbital calculations for **3Aa** were carried out by density functional theory (DFT) using B3LYP/6-31G(d).⁹ Its

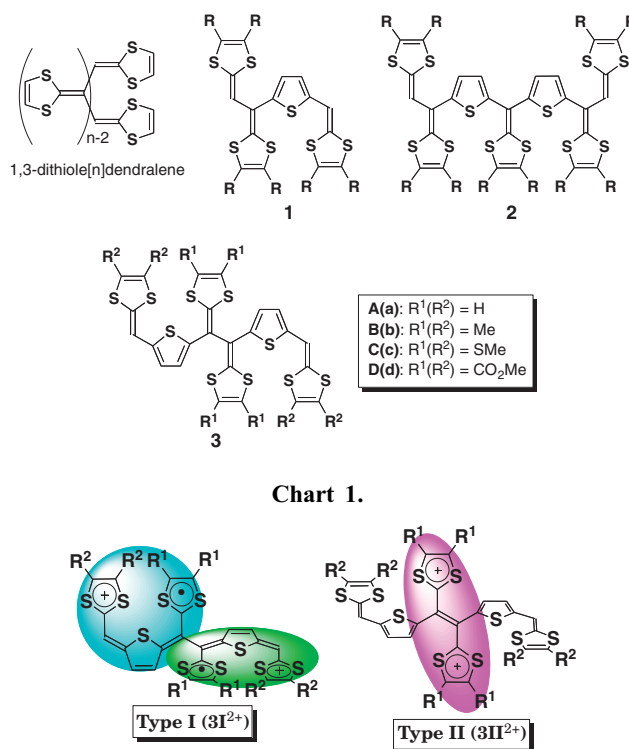
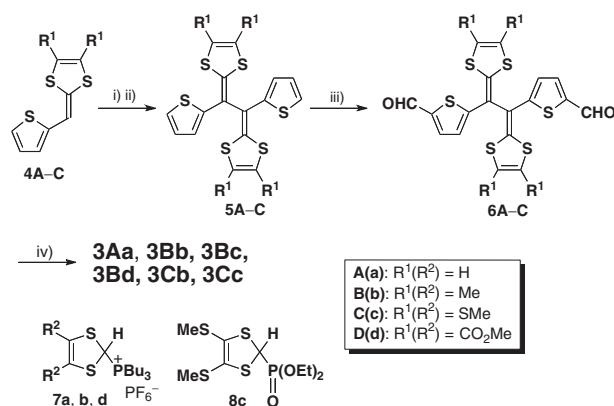


Figure 1. Plausible structures (Type I and Type II) of 3^{2+} .



Scheme 1. i) (*p*-BrC₆H₄)₃N·SbCl₆, CH₂Cl₂, ii) Zn, CH₃CN, iii) POCl₃, DMF, then NaOH, H₂O, iv) **7a**, **7b**, **7d**, or **8c**, LDA, THF, –78 °C.

optimized structure is shown in Figure 2. Each thiophene–extended TTF moiety is almost planar, which indicates that two 1,3-dithiole rings in this unit conjugate effectively with each

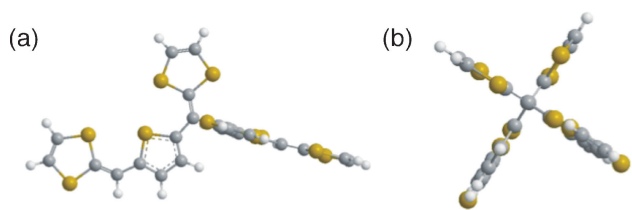


Figure 2. Optimized structures of **3Aa**; (a) top view of one of the planar thiophene-extended TTF moieties and (b) its side view.

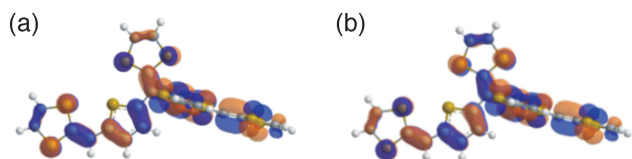


Figure 3. (a) HOMO and (b) HOMO-1 of **3Aa**. The energy levels are -4.270 and -4.325 eV, respectively.

other through the thiophene ring. On the other hand, two thiophene-extended TTF moieties are almost perpendicular, which means that they are not conjugated. The highest occupied molecular orbital (HOMO) and the next HOMO (HOMO-1) of **3Aa** are shown in Figure 3. Both the HOMO and HOMO-1 are essentially composed of the two HOMOs of thiophene-extended TTF units and delocalize over the whole molecule. The energy difference of the HOMO and HOMO-1 is only 0.055 eV, which suggests that four electron redox may occur in a narrow potential region.

The electrochemical properties of **3** were investigated by cyclic voltammetry. Their redox potentials are summarized in Table 1 together with their related compounds **5** and **9**. All the derivatives exhibited 2–4 pairs of redox waves. Comparison of the intensity of the peak currents suggests that the redox processes of **3Aa**, **3Bc**, **3Bd**, and **3Cc** involve simultaneous two or three electron oxidation. Thus, it is indicated that all the derivatives of **3** exhibit four electron redox within a narrow voltage region of 0.17 – 0.34 V ($E_4 - E_1$) as is anticipated based on the MO calculation mentioned above. The first redox process of all the derivatives except for **3Bd** corresponds to one-electron transfer (Figure 4a). Their first redox potentials are comparable to those of the corresponding derivatives of **9** (Chart 2), and are significantly lower by 0.14 – 0.17 V compared with the E_{m1} ($= (E_1 + E_2)/2$) values of the corresponding derivatives of **5**. The other redox waves are broad due to partially overlapping the remaining redox waves. On the other hand, the highest redox potentials of these derivatives are higher by 0.09 – 0.18 V than those of the corresponding derivatives of **9**. The E_1 and E_2 of **3Bc** and **3Cb** are almost the same. No substitution effect on the E_1 and E_2 suggests that the electronic structures in the monocationic and dicationic states are similar to each other between **3Bc** and **3Cb**. In contrast, two-pair of two-electron redox waves were clearly observed for **3Bd** (Figure 4b). The E_{m1} of **3Bd** (0.01 V) is a little higher by 0.04 V than the E_1 of **9Bd** (-0.03 V),¹⁰ and is identical to the E_{m1} of **5B**. This indicates that the electronic structure of **3Bd** in the dicationic states is different from those of the other derivatives. The E_{m2} of **3Bd** is higher by 0.20 V than E_2 of **9Bd**, suggesting that the

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

Donor	E_1	E_2	E_3	E_4	$E_4 - E_1$
3Aa	-0.08	0.07 (2e) ^d		0.18	0.26
3Bb	-0.16	-0.04	0.03	0.11	0.27
3Bc	-0.07	0.03	0.16 (2e)		0.23
3Bd	0.01 (2e)		0.35 (2e)		0.34
3Cb	-0.07	0.02	0.10	0.18	0.25
3Cc	0.00	0.17 (3e)			0.17
5A	0.09 (2e)				
5B	0.01 (2e)				
5C	0.14 (2e)				
9Aa	-0.11	0.00			
9Bb	-0.18	-0.06			
9Bc	-0.11	0.02			
9Bd	-0.03	0.15			
9Cc	-0.01	0.09			

^aIn PhCN containing 0.1 M Bu₄NPF₆, all potentials are measured against Ag/Ag⁺ reference electrode and converted to vs. Fc/Fc⁺. ^b $E_{m1} = (E_1 + E_2)/2$, $E_{m2} = (E_3 + E_4)/2$. ^cThree-electron-transfer process. $E_{M2} = (E_2 + E_3 + E_4)/3$. ^dThe number of electrons involving the simultaneous multi-electrons redox process is given in parentheses.

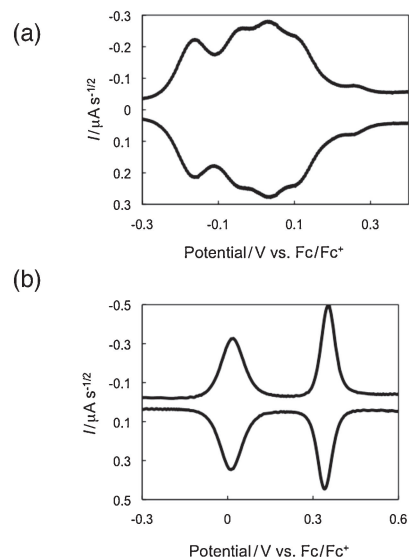


Figure 4. (a) Deconvoluted cyclic voltammograms of **3Bb** and (b) **3Bd** in benzonitrile.

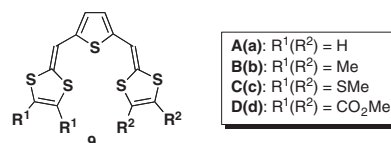


Chart 2.

electronic structure of the tetracationic state of all the derivatives of **3** bear a resemblance to each other.

Spectroelectrochemistry of **3Bc** and **3Bd** was investigated in order to elucidate the electronic structures of the oxidized

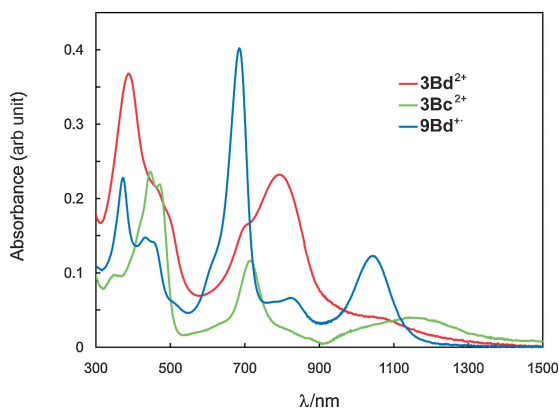
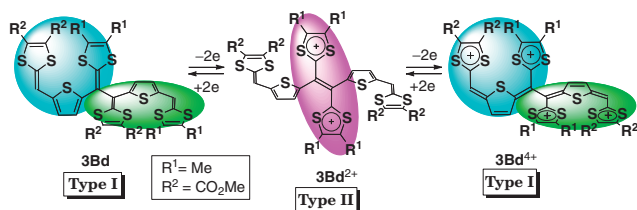


Figure 5. UV-vis-NIR spectra of **3Bd**²⁺, **3Bc**²⁺, and **9Bd**⁺ generated by applying a constant voltage of 0.20, 0.05, and 0.05 V (V vs. Fc/Fc⁺) for **3Bd**²⁺, **3Bc**²⁺, and **9Bd**⁺, respectively in benzonitrile solution.



Scheme 2. Plausible redox process of **3Bd**.

species. The UV-vis-NIR spectra of **3Bc**²⁺ and **3Bd**²⁺ in benzonitrile are shown in Figure 5 together with that of **9Bd**⁺.^{11,12} The electronic spectrum of **3Bc**²⁺ consists of absorption maxima at 356, 450, 475, 721, and 1153 nm. The dication **3Bd**²⁺ shows absorption maxima at 392, 709, and 799 nm. The large difference of the electronic spectra between **3Bc**²⁺ and **3Bd**²⁺ could be attributed to the difference in the electronic structure of the dicationic states. The spectrum of **3Bc**²⁺ has remarkable resemblance to **9Bc**⁺ ($\lambda_{\text{max}} = 729$ and 1201 nm), which indicates that two positive charges in **3Bc**²⁺ distribute separately on two thiophene-extended TTF moieties. Namely, the structure **3I**²⁺ (Type I in Figure 1) contributes significantly to the ground state of **3Bc**²⁺, and the contribution of **3II**²⁺ (Type II in Figure 1) can be negligible. An absorption maximum at 1000–1200 nm, a characteristic of **9**⁺, was not observed in **3Bd**²⁺. This result strongly indicates little contribution of the structure **3I**²⁺. Therefore, we think the “Type II” structure significantly contributes to **3Bd**²⁺.¹³ The tetracation **3Bd**⁴⁺ exhibited absorption maxima at 388, 590, and 635 nm, which resembles the spectrum of **9Bd**²⁺ (384 and 624 nm, Figure S2¹¹). Thus, **3Bd** shows drastic conformational changes among **3Bd**, **3Bd**²⁺, and **3Bd**⁴⁺ as shown in Scheme 2. On the other hand, the redox system of the other derivatives of **3** can be considered as a combination of **9**, in which two **9** units of have perpendicular position which disturbs the conjugation between them. The different redox behavior between **3Bd** and the others can be understood by consideration of the stability of their dicationic states. That is, the “Type II” structure is stabilized by four electron-donating methyl groups, while the “Type I” structure in **3Bd**²⁺ may be destabilized by electron-withdrawing methoxycarbonyl groups in the terminal 1,3-dithiole rings.

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

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- 3Aa**: 72% yield; yellow powder; mp 72–75 °C; IR (KBr): ν 2947, 2912, 1599, 1490, 1445 cm⁻¹; ¹H NMR (270 MHz, CDCl₃): δ 6.84 (2H, m), 6.77 (2H, m), 6.68 (2H, m), 6.49 (4H, d), 6.40 (4H, d); MS (MALDI) *m/z*: 621.21 (M⁺). **3Bb**: 80% yield; yellow powder; mp 88–92 °C; IR (KBr): ν 2954, 2915, 1508, 1433 cm⁻¹; ¹H NMR (270 MHz, CDCl₃): δ 6.75 (2H, d), 6.72 (2H, d), 6.52 (2H, s), 2.04 (6H, d), 2.00 (6H, d), 1.94 (6H, d), 1.90 (6H, d); MS (MALDI) *m/z*: 733.22 (M⁺). **3Bc**: 45% yield; yellow powder; mp 172–175 °C; IR (KBr): ν 2922, 2852, 1525, 1509, 1481 cm⁻¹; ¹H NMR (270 MHz, CDCl₃): δ 6.77 (4H, m), 6.57 (2H, s), 2.44 (12H, d), 2.06 (6H, s), 1.95 (6H, s); MS (MALDI) *m/z*: 860.94 (M⁺). **3Bd**: 90% yield; brown oil; IR (KBr): ν 2949, 1748, 1583, 1509, 1433 cm⁻¹; ¹H NMR (270 MHz, CDCl₃): δ 6.77 (4H, m), 6.55 (2H, s), 3.87 (12H, d), 2.07 (6H, s), 1.92 (6H, s); MS (MALDI) *m/z*: 910.38 (M⁺). **3Cb**: 22% yield; yellow powder; mp 182–185 °C; IR (KBr): ν 2952, 2922, 1637, 1526, 1509, 1482 cm⁻¹; ¹H NMR (270 MHz, CDCl₃): δ 6.77 (4H, m), 6.57 (2H, s), 2.49 (6H, s), 2.39 (6H, s), 2.01 (6H, s), 1.95 (6H, s); MS (MALDI) *m/z*: 860.89 (M⁺). **3Cc**: 84% yield; yellow powder; mp 87–91 °C; IR (KBr): ν 2914, 1559, 1523, 1475, 1420 cm⁻¹; ¹H NMR (270 MHz, CDCl₃): δ 6.81 (2H, d), 6.75 (2H, d), 6.58 (2H, s), 2.50 (6H, s), 2.44 (12H, d), 2.40 (6H, s); MS (MALDI) *m/z*: 990.47 (M⁺).
- The molecular orbital calculation was carried out using the Gaussian 03 program. M. J. Frisch, et al., *Gaussian 03*, Gaussian, Inc., Pittsburgh, PA, **2003**.
- Compounds **9Bc** and **9Bd** were newly prepared according to the literature: K. Takahashi, T. Nihira, M. Yoshifuji, K. Tomitani, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2330.
- Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- The oxidized species were generated by applying at a constant voltage in benzonitrile containing 0.1 M Bu₄NPF₆ as an electrolyte.
- In the UV-vis-NIR spectrum of **5B**²⁺, an absorption maximum appeared at 471 nm, which is significantly shorter by ca. 160 nm than that of **3Bd**²⁺ probably due to the presence of electron-donating 1,3-dithiole rings in addition to the π -electron framework of **5**.