Syntheses and Properties of Thiophene-inserted [3]Dendralenes with Redox-active 1,3-Dithiol-2-ylidene Units

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Novel dendralene type cross-conjugate molecules based on 1,3-dithiol-2-ylidene units with thiophene have been prepared. The conjugation in the oxidized stage is mainly through the thiophene core, while the cross-conjugated nature is observed in the neutral state. The CT complex of **2a** with $TCNQF_4$ shows moderated electrical conductivity of $10^{-4}\ S\,cm^{-1}$.

The cross-conjugated systems with 1,3-dithiole rings are of interest as novel multistage redox systems as well as donor component for organic conductors.[1–4] Their unique conjugation patterns derived from cross-conjugate topologies are also subject to potential application for soliton valve and switch in molecular electronic devices.[5] Therefore, control of the conjugation pathway and modulation of the strength in cross-conjugated systems with multistage redox are very important. The [3]dendralene with 1,3-dithiole rings **1** (Chart 1) is one of the most basic cross-conjugation systems with redox-active sites. It has a novel nonplanar structure; namely, one of the terminal 1,3-dithiole ring is almost orthogonally distorted, whereas the remaining vinylogues TTF moiety is nearly planar.[4] In this connection, the unsymmetrically cross-conjugated system **2** containing thiophene inserted vinylogue **3**[6] is of considerable interest, because the central thiophene core may act as a conjugation "valve" through the building parts **3** and **4**.[7] In this letter, we report herein the syntheses, electronic structure, and electrochemical properties of thiophene-inserted unsymmetrical dendralene derivatives **2**.

The synthetic route toward **2** is shown in Scheme 1. The Vilsmeier–Haack reaction on 6-thienyl-1,4-dithiafulvalenyl derivatives **5b** and **5c**[7] gave the bisformylated products **6b** and **6c** in 13 and 27% yields, respectively. The conversion to **6a** was achieved in 98% yield by demethoxycarobonylation of **6b** in HMPA at 90–130 °C in the presence of $LiBr{\cdot}H_2O$. Treatment of **6a**–**6c** with corresponding phosphonate ester **7a** and **7c** or phosphonium salt **8** in the presence of BuLi at −78 °C gave the target molecules **2a**–**2d** in 25–75% yields.

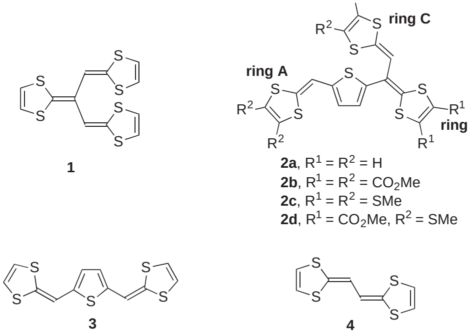
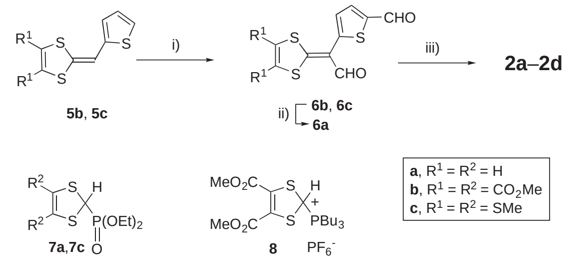


Chart 1.



Scheme 1. i) $POCl_3$, DMF, then HCl ii) $LiBr{\cdot}H_2O$, HMPA, 90–130 °C, iii) **7a**, **7c**, or **8**, BuLi, THF, −78 °C.

The molecular orbital calculation of **2a** has been carried out by using B3LYP/6-31G(d) method.[8] Figure 1 shows the optimized geometry of **2a** with the HOMO, the HOMO−1, and the LUMO. The optimized geometry of **2a** adopts a twisted structure composed of the thiophene with the dithiole unit (ring A) and the transoid vinylogue part (rings B and C). The dihedral angle between the thiophene and the outer dithiole ring (ring A) is 10.4°, while the dihedral angles between the thiophene and the other two dithiole rings are 42.7° for ring B and 88.8° for ring C, respectively. In contrast, the dihedral angle between two dithiole rings in the vinylogue part (rings B and C) is 28.9°, which is smaller than that of thiophene and the ring B (42.7°). The above results suggest that **2a** has basically cross-conjugate nature between the building brocks of **3** and **4**. However, the conjugation derived from **4** may be stronger than that from **3** in this cross-conjugated system.

Figure 2 shows UV–vis spectra of **2a** and its related compounds **3** and **4** measured in dichloromethane. The compound **2a** exhibits three absorption maxima at 388, 422, and 446 nm. The wavelengths of absorption maxima and their molar extinction coefficients of **2a** are closed to those of **3** and **4**, indicating cross-conjugation composed of the moieties **3** and **4**.

The redox properties of **2** and related compounds have been investigated by cyclic voltammetry in PhCN. Their redox potentials are listed in Table 1 together with [3]dendralene **1**.[3a] All the dendralenes **2a**–**2d** showed two reversible redox waves and additional one quasi-reversible redox wave. The positive

Figure 1. (a) HOMO, (b) HOMO−1, and (c) LUMO of **2a**.

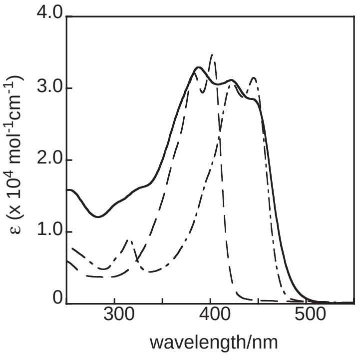
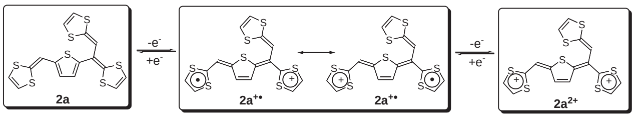


Figure 2. UV–vis spectra of **2a** (solid line), **3** (dash-dotted line), and **4** (broken line) in dichloromethane.

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

Donor	$E_1{}^{1/2}$/V	$E_2{}^{1/2}$/V	$E_3{}^{1/2}$/V	$E_2 - E_1$/V
2a	−0.12	0.02	0.50[b]	0.14
2b	0.29	0.36	0.82[b]	0.07
2c	−0.03	0.09	0.42[b]	0.12
2d	0.08	0.25	0.43[b]	0.17
3	−0.11	0.00	—	0.11
4	−0.17	0.05	—	0.22
1[c]	−0.20	−0.06	0.86	

[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]Quasi-reversible process. [c]From ref 3a. In PhCN, 0.1 M Bu_4NClO_4, vs. Fc/Fc^+.



Scheme 2. Possible oxidation process of **2a**.

shifts of the E_1 and E_2 in **2b** and **2c** compared with **2a** are attributed to their terminal substituents. Interestingly, the first and second redox potentials of **2a** are very similar to those of **3**, while the first redox potential of **4** is very close to that of [3]dendralene **1**. These results suggest that the charges of oxidized species mainly distribute on the moiety **3** rather than **4** (Scheme 2).

Electronic spectra of oxidized state of **2a** in PhCN were measured at −0.10 and 0.15 V (vs. Fc/Fc^+).[9] The electronic spectrum at −0.10 V measured in the range from 300 to 1100 nm showed low energy absorption maxima corresponding to $\mathbf{2a}^{+\bullet}$ at 584, 700, and 755 (sh) nm. The pattern of the spectrum is similar to that of a derivative of $\mathbf{3}^{+\bullet}$.[6b] Because of the nonplanar molecular structure of **2a**, intermolecular interaction may be ruled out. Hence, the absorption is concluded to be characteristics of electronic structure in mixed-valence (MV) state between two dithiole rings in the thiophene-inserted vinylogue part.[6b] The spectrum at 0.15 V clearly showed dication species in PhCN solution. The absorption maximum at 870 nm indicates the conjugation of thiophene backbone, i.e., building block **3**, in dication.[6b]

The $TCNQF_4$ complex based on **2a** was prepared by mixing of the donors with $TCNQF_4$ in dichloromethane–acetonitrile solution. The electronic spectrum of **2a**•$TCNQF_4$ complex was similar to that of $\mathbf{2a}^{+\bullet}$ generated by an electrochemical oxidation,[9] suggesting the donor is almost fully oxidized in the complex. It showed a moderate conductivity of $\sigma_{rt} = 2.0 \times 10^{-4}\,S\,cm^{-1}$ on a compressed pellet. The further investigation, in particular, preparation of single crystal of molecular conductors based on the cross-conjugate system **2** is actively underway.

In conclusion, new cross-conjugation molecules with multistage redox-active sites have been synthesized. The thiophene insertion into [3]dendralene causes different conjugation patterns in each redox state. Namely, in the neutral state, the cross-conjugation of **3** and **4** is observed. In contrast, the moiety **3** mainly contributes to the conjugation in oxidized stage. Furthermore, the first conducting molecular complex based on the dendralene system has been demonstrated.

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

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