Oxidation of Unsymmetrically Substituted Quaterthiophene with Two Terminal Ferrocenyl Groups

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An unsymmetrically substituted quaterthiophene with two terminal ferrocenyl groups was prepared as a long π-conjugated system. Electrochemical and spectroscopic studies were carried out to evaluate the electronic and/or electrostatic communication between the two terminals. The one-electron oxidation would occur at one ferrocene moiety specified due to the unsymmetry of the oligothiophene moiety. The one-electron oxidizing species extended into the oligothiophene moiety apparently interacts with the other terminal ferrocene moiety.

Long π-conjugated systems are of interest for their electronic and redox properties. In order to clarify and modify the properties, the introduction of redox-active terminals into the systems is effective. Furthermore, multiple introduction enables investigation of electronic and/or electrostatic communication between the terminals via the conjugated systems.[1] Ferrocene is well known as a highly stable compound in both the oxidized and neutral states and thus appropriate for the terminals. Several researchers have prepared diferrocenyl conjugated systems,[2–5] which should be regarded as π-conjugated systems with two terminals. Unfortunately, a considerable number of the compounds showed no communication between the two terminals; for example 1,4-diferrocenylbenzene[3a] and diferrocenyldihexylterthiophene.[3b] All the diferrocenyl compounds are symmetric in structure and the two terminals are equivalent entirely. Groups substituted on π-conjugated systems significantly affect the electronic structures of the systems, suggesting that one can control the oxidation processes or the oxidation states of the conjugated systems. In this paper, we report an unsymmetrically substituted quaterthiophene with two terminal ferrocenyl groups (**1**) and with one or no terminal ferrocenyl group (**2**–**4**) (Chart 1). The two terminal ferrocenyl groups of **1** are nonequivalent because of linkage with the unsymmetrically substituted quaterthiophene moiety.

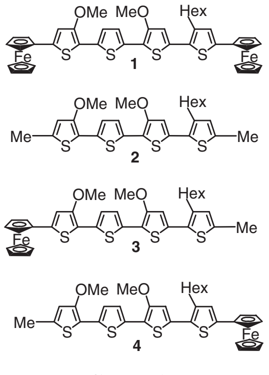

Chart 1.

In the synthesis of the quaterthiophene derivatives **1**–**4**, the quaterthiophene moieties were prepared by the Migita–Kosuge–Stille coupling of tributylstannyldimethoxyterthiophene or the α-methyl derivative with 2-bromo-3-hexylthiophene or the α-methyl derivative, and then the obtained quaterthiophenes were iodized and finally coupled with ferrocenylzinc chloride. Detailed synthetic procedures are described in Supporting Information.[6]

Oxidation of the quaterthiophene derivatives **1**–**4** was investigated by cyclic voltammetry (CV), square wave voltammetry (SWV), and controlled potential coulometry (CPC). The electrochemical measurements were carried out in dichloromethane solutions containing 2.0×10^{-3} M of each compound and 0.1 M of Bu_4NClO_4. The electrochemical measurements were referenced against ferrocenium/ferrocene (Fc^+/Fc) as the internal standard. The oxidation potentials (E_{ox}) and coulometric n-values (n_a) of the quaterthiophene derivatives and ferrocene were obtained by the CV measurements (Figures 1a and S1–S4)[6] and CPC measurements, and summarized in Table 1.

The E_{ox} of ferrocene was 0.00 and 0.06 V lower than the first of a dimethyl end-capped quaterthiophene derivative **2**, indicating that in ferrocenyl quaterthiophene derivatives **1**, **3**, and **4** the ferrocene moieties are more oxidizable than the quaterthiophene

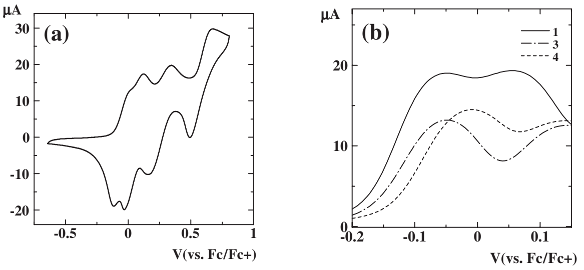

Figure 1. (a) Cyclic voltammogram of **1**. (b) Square wave voltammograms of **1**, **3**, and **4**.

Table 1. Electrochemical data of ferrocene and **1**–**4**

Compound	$E_{ox}^{1\ a}$ /V	$n_a^{1\ b}$ /F mol^{-1}	$E_{ox}^{2\ a}$ /V	$n_a^{2\ c}$ /F mol^{-1}	$E_{ox}^{3\ a}$ /V	$E_{ox}^{4\ a}$ /V
Ferrocene	0.00	1.0	—	—	—	—
1	−0.05	—[d]	0.05	2.3	0.27	0.59
2	0.06	—	0.38	—	—	—
3	−0.05	1.1	0.14	2.2	0.54	—
4	−0.01	1.2	0.14	2.2	0.47	—

[a] E_{ox}^{n} are the n-th oxidation potentials. [b] n_a^1 are coulometric n-values for the first oxidation. [c] n_a^2 are coulometric n-values up to the second oxidation. [d] The value is uncertain on account of overlapping of waves.

moieties. The dimethyl **2** had two E_{ox}s corresponding to the successive generation of the radical cation and dication, as previously reported for long oligothiophenes.[7] The cyclic voltammogram of the diferrocenyl **1** revealed four reversible redox waves (Figure 1a). The two lower waves were observed opposite each other at 0.00 V, the E_{ox} of ferrocene. In addition, the n_{a} up to the second oxidation was $2.3\,\mathrm{F\,mol^{-1}}$ (two-electron oxidation). These results indicate that the two lower redox waves at $E_{\mathrm{ox}}\mathrm{s} = -0.05$ and 0.05 V and the two higher waves at $E_{\mathrm{ox}}\mathrm{s} = 0.26$ and 0.58 V are assigned to the oxidation of the two ferrocene moieties and the two stepwise oxidation of the quaterthiophene moiety, respectively. For the monoferrocenyl derivatives **3** and **4**, three reversible redox waves were detected (Figures S3 and S4)[6] and the n_{a}s up to the first were 1.1–$1.2\,\mathrm{F\,mol^{-1}}$ (one-electron oxidation). These results suggest that the lowest redox waves (at $E_{\mathrm{ox}} = -0.05$ V for **3** and $E_{\mathrm{ox}} = -0.01$ V for **4**) and the two higher waves (at $E_{\mathrm{ox}}\mathrm{s} = 0.14$ and 0.54 V for **3**, and $E_{\mathrm{ox}}\mathrm{s} = 0.14$ and 0.47 V for **4**) are attributed to the oxidation of the ferrocene moieties and the two stepwise oxidation of the quaterthiophene moieties, respectively.

Figure 1b displays the square wave voltammograms of **1**, **3**, and **4** in the voltage range from −0.20 to 0.15 V. The peak potentials of the waves agreed within limits of error with the corresponding E_{ox}s obtained by CV. The waves attributable to the oxidation of the ferrocene moieties in **3** and **4** were observed at −0.05 and −0.01 V, respectively. Both the peak potentials are shifted from the E_{ox} of ferrocene, 0.00 V, and the degrees of the shifts are apparently different. These results demonstrate that the intensity of the interaction between the two neighboring moieties, the ferrocene moiety and the quaterthiophene moiety, would depend on the substituted position of the ferrocenyl group on the unsymmetric quaterthiophene moiety; the α-position of the end methoxythiophene ring for **3** and the α-position of the end hexylthiophene ring for **4**. The voltammogram of **1** shows two waves at −0.05 and 0.05 V assignable to the oxidation of the two ferrocene moieties. The peak potential of the one wave (at −0.05 V) agrees with that of the wave due to the ferrocene moiety in **3**, however, the peak potential of the other (at 0.05 V) is clearly higher than that of the wave due to the ferrocene moiety in **4** (at −0.01 V). That is, the two peak potentials, the E_{ox}s, of the ferrocene moieties in **1** are not completely consistent with the combination of the peak potentials, the E_{ox}s, of the ferrocene moieties in **3** and **4**. The inconsistence of the potentials leads us to infer that the two terminal ferrocenyl groups in **1** interact with each other. Further, the agreement of the first E_{ox} of the ferrocene moiety in **1** and the E_{ox} of the ferrocene moiety in **3** implies that the one-electron oxidation of **1** occurs at the ferrocene moiety that is attached to α-position of the end methoxythiophene ring and the interaction between the ferrocene moieties in **1** does not take place in the neutral state but in one-electron oxidized state.

To elucidate the oxidized state of **1**, a stoichiometric amount of $FeCl_3$ was added to a dichloromethane solution containing 2.0×10^{-3} M of each **1** and **2** and then the chemically oxidized solutions were subjected to electronic absorption spectral analysis. Figure 2 shows the spectra of **1** and **2** in neutral and one-electron oxidized states. The spectrum of neutral **1** has a π–π^* transition band at 2.8 eV.

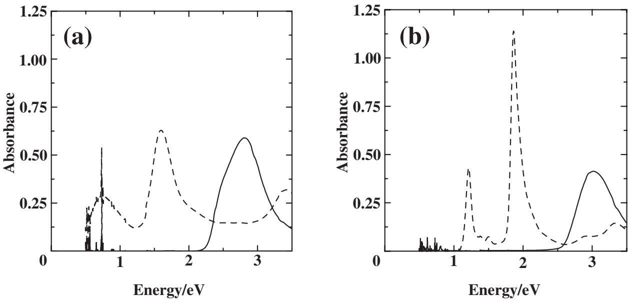

Figure 2. Electronic absorption of (a) **1** and (b) **2**: neutral (solid line) and one-electron oxidized (dashed line).

The one-electron oxidation of **1** resulted in a remarkable decrease of the π–π^* transition band, accompanied by the appearance of two strong bands at 1.6 and 0.7 eV. This spectral change during one-electron oxidation resembles those of **2** and previously reported oligothiophene derivatives,[7] being interpreted as the generation of a cation radical (polaron). These results evidenced the presence of an oxidizing species such as a cation radical in the quaterthiophene moiety of one-electron oxidized **1**. Therefore, the one-electron oxidizing species does not remain in the one ferrocene moiety of **1**, but spreads over the ferrocene and the quaterthiophene moieties, and then would coulombically interact with the other ferrocene moiety.

In summary, an unsymmetrically substituted quaterthiophene with two terminal ferrocene groups, **1**, was prepared as a long π-conjugated system with two redox active terminals. The electrochemical and optical properties were compared with those of a series of the quaterthiophene derivatives, **2**–**4**. The results show that the one-electron oxidation of **1** would occur at the ferrocene moiety attached to the end methoxythiophene ring and the resulting oxidizing species extends to the neighboring quaterthiophene moiety. The extended oxidizing species would electrostatically interact with the other terminal ferrocene moiety. The present results demonstrate the effectiveness of substituents on the quaterthiophene moiety for controlling the oxidation process in long conjugated systems having terminals.

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

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