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Oxidation of Dihedral-angle-controlled 2,2′-Bithiophenes with Terminal Ferrocenyl Groups

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Novel dihedral-angle-controlled 2,2′-bithiophenes with terminal ferrocenyl groups have been designed and prepared. The electrochemical and spectroscopic properties indicated that the interaction between the terminal ferrocene moieties was distinctly affected by the twist in the π-conjugated system.

During recent decades, π-conjugated materials have attracted much attention due to their potential applicability in optical and electrical devices. Among π-conjugated materials, oligothiophene and its derivatives have been extensively studied because of their excellent environmental stability in both neutral and oxidized states.[1] Furthermore, it clarifies the function of the π-conjugated systems in detail to introduce redox centers, such as ferrocene,[2] at termini of the systems. Some papers have reported the preparation and properties of multiple ferrocenyl-oligothiophenes and investigated the interaction, the electronic or electrostatic communication, between the terminal ferrocene groups.[3–10] The interaction decays with increasing metal–metal distance.[3,11] We synthesized diferrocenyldimethoxyterthiophene[5] and diferrocenyldihexylterthiophene.[12] The comparison of their redox process showed that the interaction between the terminal ferrocenyl groups is intensively affected by substituents on the π-conjugated system.[13]

In this letter, dihedral-angle-controlled 2,2′-bithiophenes with terminal ferrocenyl groups, 4,4-diethyl-2,6-diferrocenylcyclopenta(2,1-*b*:3,4-*b*′)dithiophene (C1FF) and 2,9-diferrocenylcycloocta(2,1-*b*:3,4-*b*′)dithiophene (C4FF) were prepared, and their electrochemical and optical properties were examined (Chart 1). The 2,2′-bithiophene moiety in C1FF is linked with a methylene bridge between 3- and 3′-carbons, being almost planer, whereas the moiety in C4FF is bridged with 1,4-butane, deviating from planarity, and convenient for easy preparation. In addition to the differocenyl derivatives, monoferrocenyl derivatives; 4,4-diethyl-2-ferrocenyl-6-hexylcyclopenta(2,1-*b*:3,4-*b*′)-dithiophene (C1FH) and 2-ferrocenyl-9-hexylcycloocta(2,1-*b*:3,4-*b*′)dithiophene (C4FH), and non ferrocenyl derivatives; 4,4-diethyl-2,6-dihexylcyclopenta(2,1-*b*:3,4-*b*′)dithiophene (C1HH) and 2,9-dihexylcycloocta(2,1-*b*:3,4-*b*′)dithiophene (C4HH), were investigated as reference compounds for detailed discussion (Chart 1).

4,4-Diethylcyclopenta(2,1-*b*:3,4-*b*′)dithiophene and its hexyl derivative, the bithiophene moieties of the series of C1 (C1FF, C1FH, and C1HH), were synthesized according to a similar method reported by Vanderzande and co-workers.[14] Cycloocta(2,1-*b*:3,4-*b*′)dithiophene, the bithiophene moiety of the series of C4 (C4FF, C4FH, and C4HH), was prepared by the coupling of 3-bromothiophene and 1-bromo-4-(3-thienyl)-butane.[15] The obtained cycloalkadithiophenes were converted to the final products analogously to the synthesis of diferrocenyldimethoxyterthiophene[5] or dihexylterthiophene.[13] Detailed synthetic procedures are described in Supporting Information.[16]

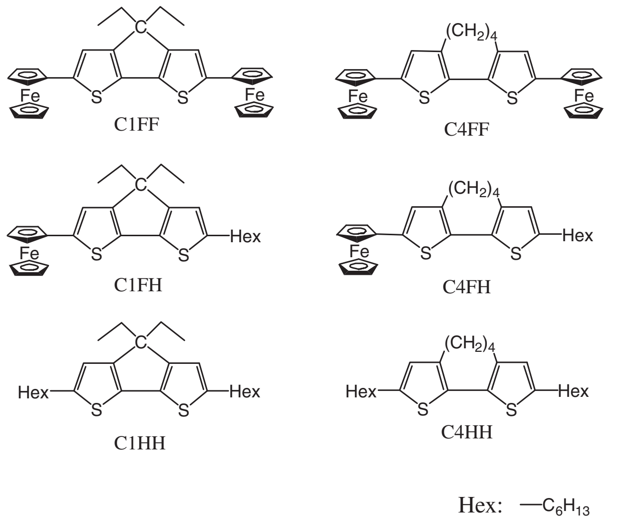

Chart 1. Dihedral-angle-controlled 2,2′-bithiophene derivatives.

The molecular structures of C1FF and C4FF were calculated using Gaussian 09.[17] Geometry optimization was performed using B3LYP/6-31G(d) integrated polarizable continuum model, which is assumed for dichloromethane. The theoretical calculation shows that the π system of bithiophene moiety in C1FF has almost flat configuration; the dihedral angle between the thiophene rings is 0.23°, and then that in C4FF has a distinctly twisted configuration; the dihedral angle is 50.03°. Oxidation of the two series of C1 and C4 was investigated by cyclic voltammetry, square wave voltammetry, and controlled potential coulometry (CPC). The electrochemical measurements were carried out in dichloromethane solutions containing ca. 2×10^{-3} M each compound and 0.1 M Bu_4NClO_4. The electrochemical measurements were referenced against ferrocenium/ferrocene (Fc^+/Fc) as the internal standard.

Figures 1 and 2 show the cyclic voltammograms (CV) and square wave voltammograms (SWV) of the ferrocenyl derivatives, C1FF, C1FH, C4FF, and C4FH. The oxidation potentials (E_{ox}) were obtained by Gaussian curve fitting of SWV, and coulometric *n* values (n_{ox}) were calculated from the CPC data, and summarized in Table 1.

Ferrocene and dihexyl derivatives C1HH and C4HH have one E_{ox} at 0.00 V and at remarkably high potentials (0.36 V for C1HH and 0.66 V for C4HH) in the electrolysis window, respectively.[16] In the ferrocenyl derivatives, the ferrocene moieties would be more readily oxidizable than the bithiophene moieties. The ferrocenyl derivatives have one E_{ox} or two E_{ox}'s, the potentials being around 0.0 V. In addition, each total n_{ox} for their oxidation agrees with the number of terminal ferrocene moiety, ca. 1 F mol^{-1} for the monoferrocenyl derivatives and

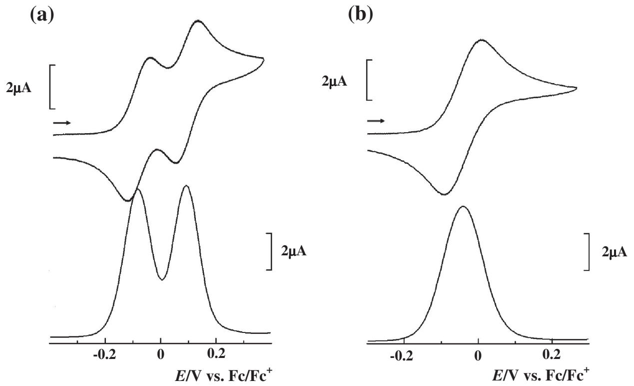

Figure 1. Cyclic voltammograms and square wave voltammograms of C1FF (a) and C1FH (b).

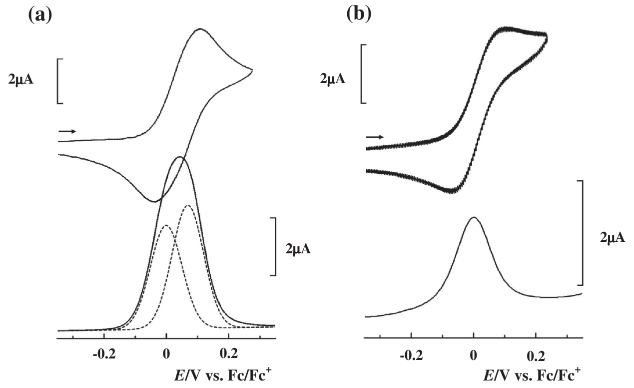

Figure 2. Cyclic voltammograms and square wave voltammograms of C4FF (a) and C4FH (b). The dashed line shown in (a) donates the Gaussian fit of the voltammogram.

Table 1. Electrochemical data of ferrocene and dihedral-angle-controlled 2,2′-bithiophene derivatves

Compound	E^{1}_{ox}[a] /V	n^{1}_{a}[b] /F mol^{-1}	E^{2}_{ox}[a] /V	n^{2}_{a}[b] /F mol^{-1}	E^{3}_{ox}[a] /V
Ferrocene	0.00	1.1	—	—	—
C1FF	−0.08	1.2	0.09	2.4	0.71
C1FH	−0.04	1.2	0.53	—	—
C1HH	0.36	—	—	—	—
C4FF	0.00[c]	—	0.08[c]	2.4	0.90
C4FH	0.00	1.1	—	—	—
C4HH	0.66	—	—	—	—

[a] E^{n} are n-th oxidization potentials. [b] n^{n}_{a} are Coulometric n value for the n-th oxidization. [c] Each value was obtained by curve fitting.

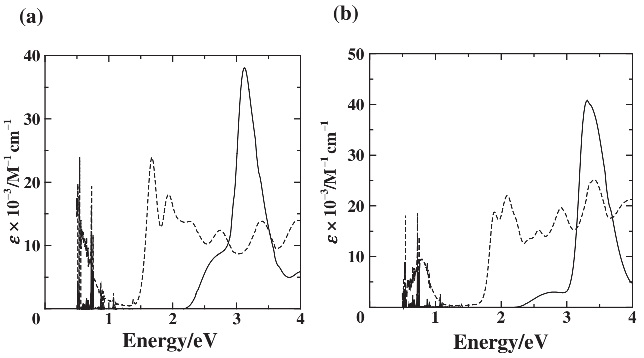

Figure 3. Electronic absorption spectra of neutral and oxidized C1FF (a) and C1FH (b). Neutral spacies (solid line), one-electron-oxidized one (dashed line).

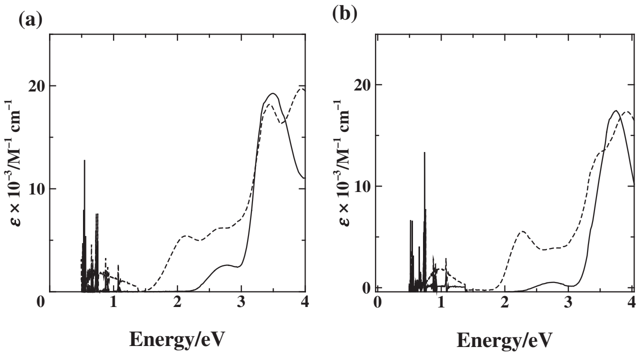

Figure 4. Electronic absorption spectra of neutral and oxidized C4FF (a) and C4FH (b). Neutral spacies (solid line), one-electron-oxidized one (dashed line).

ca. 2 F mol^{-1} for the diferrocenyl derivatives. These results imply that the observable oxidation waves in the mono- and diferrocenyl derivatives are assigned to the oxidation of ferrocenyl moieties. The oxidation wave of C4FF was apparently observed as only one wave; however, the peak separation using the curve fitting for the wave revealed two peaks at 0.00 and 0.08 V, which correspond to each E_{ox} of two terminal ferrocene moieties. On the other hand, the same procedure for the oxidation waves of the monoferrocenyl derivatives, dihexyl derivatives and ferrocene shows no peak separation. The oxidation of the two terminal ferrocene moieties in both the diferrocenyl derivatives shows a two-step process. This is interpreted in terms of the interaction between the terminal ferrocene moieties in the one-electron-oxidized states.

The first E_{ox}'s of the ferrocenyl derivatives of C4-series, C4FF and C4FH, are 0.00 V, the same as that of ferrocene. Considering the strong relationship between the electronic structure and the E_{ox}, this result indicates that the ferrocene moieties in C4FH and C4FF are electronically independent or have negligible interaction with the other moieties in the neutral states. In contrast, the first E_{ox}'s of the ferrocenyl derivatives of C1-series are −0.08 V for C1FF and −0.04 V for C1FH, much less than ferrocene. The value for C1FF is half that of C1FH. These results indicate that the ferrocene moieties in neutral C1FH and C1FF definitely electronically interact with adjacent bithiophene moieties and that the ferrocene moiety in neutral C1FF is additionally done with the other ferrocene moiety.

Ferrocene and the bithiophenes were chemically oxidized with a stoichiometric quantity of $FeCl_3$ in dichloromethane. The oxidation was achieved by addition of $FeCl_3$ to the solution containing 2.8×10^{-5} M each compound. Figures 3 and 4 show the electronic absorption spectra of the neutral and one-electron-oxidized ferrocenyl derivatives.

Neutral C1HH and C4HH have a π–π^{*} transition band at 3.7 and 4.2 eV, respectively.[16] The neutral ferrocenyl derivatives have a strong π–π* transition band at more than 3.0 eV, and then a d–d transition band at about 2.7–2.8 eV which are assigned to ferrocene moieties and are weak due to the forbidden nature. The series of C1 has a π–π* transition band at lower energy than the corresponding series of C4, exhibiting that the C1 series has a longer effective conjugation length than the C4 series.

When C1FF and C1FH are one-electron-oxidized, the π–π* transition bands reduce and two absorption bands appear below 3.0 eV: one broad band with fine structures in a wide range from 1.5 to 3.0 eV and the other band less than 1.0 eV (less than 0.5 eV for C1FF and at 0.8 eV for C1FH). The bands above 3.0 eV (3.4 and 4.0 eV) would be mainly attributable to iron(III) chloride and related substances, such as iron(II) chloride. The that of one-electron oxidation of C4FF and C4FH results in the appearance of two broad and weak bands (at 0.80 and 2.14 eV for C4FF and at 0.99 and 2.23 eV for C4FH). Further, the absorption pattern of two-electron-oxidized C4FF is similar to that one-electron oxidation, shown in Supporting Information.[16] The spectra of all the ferrocenyl derivatives in one-electron-oxidized states exhibit two absorption bands. The series of C1 has considerably strong and sharp peaks, and the spectral patterns are similar to that of diferrocenyldimethoxyterthiophene,[5] which shows the strong interaction between the terminal ferrocenyl moieties in one-electron-oxidized states. In contrast to the series of C1, those of C4 has weak and broad peaks, and the spectra are similar to that of diferrocenyldihexylthiophene,[12] which shows the weak interaction between the terminal ferrocene moieties in one-electron-oxidized states.

In summary, two dihedral-angle-controlled 2,2′-bithiophenes with terminal ferrocenyl groups were designed and synthesized. Electrochemical and spectroscopic studies were carried out to evaluate the interaction between the two terminals. The first oxidation potentials of the ferrocenyl derivatives reveal that a ferrocene moiety in neutral C1FF perturbs not only the adjacent bithiophene moiety but the other ferrocene moiety, whereas a ferrocene moiety in neutral C4FF does not clearly interact even with the adjacent bithiophene moiety. The oxidation process of C1FF and C4FF suggests the interaction between terminal ferrocene moieties in one-electron-oxidized sates. These data lead us to conclude that the terminal ferrocene moieties in C1FF would communicate electronically and that those in C4FF might interact electrostatically. Further, the electronic spectra of the ferrocenyl derivatives in one-electron-oxidized states exhibit different patterns between two series of C1 and C4, supporting the conclusion derived from electrochemical data. The present results demonstrate the distinct effectiveness of the intramolecular torsion in π-conjugation systems for controlling the charge transfer in the system. We are still working on the preparation of other dihedral-angle-controlled bithiophenes.

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