Oxidized States of Methoxy-sexithiophene Derivative with Ferrocenyl Groups

Masa-aki Sato* and Kazuhiko Fukui
Faculty of Maritime Science, Kobe University, 5-1-1 Fukae-minami, Higashinada, Kobe 658-0022

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Methoxy-sexithiophene derivative with two ferrocenyl terminal groups was prepared as a model compound for molecular wires. The oxidation process and the oxidized states of the model compound were investigated by cyclic voltammetry, coulometry, and electronic absorption spectroscopy. The first oxidation occurs in a ferrocene moiety, terminal, and the resultant oxidized species strongly interacts not only with the methoxy-sexithiophene moiety, but also with the other ferrocene.

A greate deal of research has been devoted to the study of π-conjugated polymers, because these polymers show high electric conductivities in oxidized states.[1] Molecular electronics has been proposed as a promising application for the conducting polymers. In the case of molecular electronics, the conducting polymer plays a role of a molecular wire and is required to transport charges within a single molecule.[2] Several researchers prepared diferrocenyl-polyenes,[3] diferrocenyl-arenes,[4] and diferrocenyl-cumulenes,[5] which should be regarded as model compounds for molecular wires with two terminals. The electronic interaction between the terminals was detected up to six-conjugated double bonds but decayed with increasing metal–metal distance. Recently, we have synthesized an alkyl-sexithiophene derivative with two ferrocenyl groups, a model compound containing a longer molecular wire.[6] No evidence for the electronic interaction between the ferrocene moieties was found. Nevertheless, a ligand-to-metal charge-transfer (LMCT) band was observed in the absorption spectra of the chemically oxidized alkyl-sexithiophene derivatives.[6,7] When the charge, oxidized species, in the oligothiophene moieties is stabilized, one can expect the electronic interaction between terminals via longer molecular wires. Miller et al. have reported that methoxy groups substituted on each end ring of oligothiophenes give stable oxidized species.[8] In this paper, we report ferrocenyl end-capped dimethoxy-sexithiophene (**1**) as a model compound consisting of a long molecular wire and two terminals, and methyl end-capped dimethoxy-sexithiophene (**2**) as a reference compound (Chart 1). The compounds were substituted with hexyl groups to enhance the solubility for preparation and measurements in solutions. The oxidation process and the oxidized states of the compounds were investigated to elucidate the electronic interaction between both the terminals via the wire.

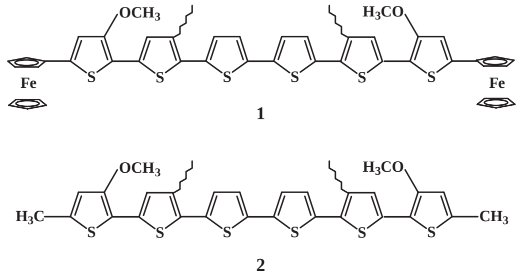

Chart 1.

The ferrocenyl and methyl end-capped **1** and **2** were prepared using dihexylquaterthiophene as a starting material analogously to the synthesis of ferrocenyl end-capped dimethoxy-terthiophene.[4b]

The electrochemical measurements were carried out in dichloromethane solutions containing 2.0×10^{-3} M of each compounds and 0.1 M of tetrabutylammonium perchlorate. The measurement cell had a three-electrode set-up (Pt working and counter electrode, Ag/Ag^+ reference electrode) and the measurements were referenced against ferrocenium/ferrocene (Fc^+/Fc) as the internal standard. In cyclic voltammograms, the potential was swept at a rate of 100 mV/s. The controlled potential coulometry of the oxidation waves was conducted at 0.2 V vs Fc^+/Fc, using a two-compartment cell. The electrochemical data are summarized in Table 1. The cyclic voltammograms of ferrocene and **2** revealed one and two reversible redox waves, respectively. Compound **2** formed stably both cation radicals and dications in this measurement range, as reported for long oligothiophenes.[8,9] The redox potential of ferrocene is lower than the first one of **2** by 60 mV, showing that the ferrocene is more oxidizable. The cyclic voltammogram of **1** is displayed in Figure 1. Although all the peak separation is not clear, it is possible to pick up three pairs of redox waves in the voltammogram as marked in the figure. Each redox wave is broad and exhibits a large difference between the anodic and cathodic peak potentials ($E_{p,a} - E_{p,c}$) in comparison with those of ferrocene and **2**. These features may be due to the significant change in the molecular structure during the redox processes. The first

Table 1. Data from cyclic voltammetry and controlled potential coulometry

Compound	$E^1{}_{1/2}{}^a$ /V	E^1p,a − E^1p,c^b /mV	$n^1{}_a{}^c$ /Faradays·mol^{-1}	$E^2{}_{1/2}{}^a$ /V	E^2p,a − E^2p,c^b /mV	$n^2{}_a{}^d$ /Faradays·mol^{-1}	$E^3{}_{1/2}{}^a$ /V	E^3p,a − E^3p,c^b /mV
Ferrocene	0.00	130	1.1	—	—	—	—	—
1	−0.07	260	—^{e}	0.01	230	2.2	0.14	290
2	0.06	100	1.0	0.26	90	2.1	—	—

[a] $E^n{}_{1/2}$ are the nth redox potentials. [b] $E^n{}_{p,a}$ and $E^n{}_{p,c}$ are the nth anodic and the nth cathodic peak potentials, respectively. [c] $n^1{}_a$ are coulometric n-values for the first oxidation. [d] $n^2{}_a$ are coulometric n-values up to second oxidation. [e] The value is uncertain on account of overlapping waves.

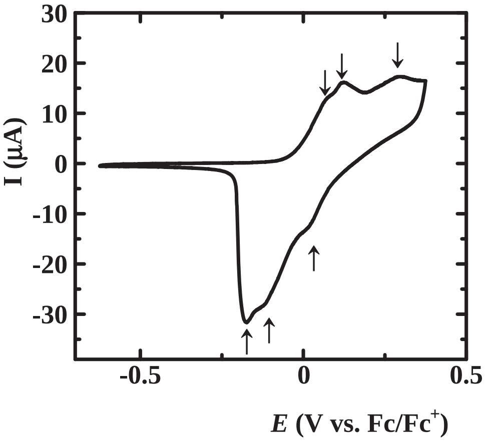

Figure 1. Cyclic voltammogram of **1**.

and second redox waves of **1** were observed at nearly the same potential as the redox wave of ferrocene, and at lower than that of the first redox wave of **2**. In addition, the coulometric n-value (n_a) up to the second oxidation was 2.2 faradays per mole (two-electron oxidation). These results indicate that the first and second redox waves of **1** correspond to the interconversion between ferrocene and ferrocenium ion in the molecule. The splitting of the redox waves for the ferrocene moieties suggests a strong interaction between the two terminal ferrocene moieties, which would be associated with Fe(II)Fe(III) mixed-valent states. The third redox wave at a higher potential would be related to the sexithiophene moiety.

Ferrocene, **1**, and **2** 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 of each compound. The electronic absorption spectra of neutral and one-electron-oxidized ferrocene demonstrated no distinct band because of their small optical densities. The neutral **2** has a π–π^* transition band at 2.9 eV. The one-electron oxidation of **2** resulted in the remarkable decrease of the π–π^* transition band and the appearance of two strong bands at 1.5 and 0.7 eV. This spectral change during one-electron oxidation resembles those of previously reported alkyl- and methoxy-sexithiophenes,[8,10] being interpreted by the generation of a cation radical (polaron). Figure 2 shows the electronic absorption spectra of neutral and one-electron oxidized **1**. The spectrum of neutral **1** exhibits a π–π^* transition band at 2.7 eV. This value is smaller than that of **2**, indicating that **1** possesses a longer effective conjugation length by the interaction between the sexithiophene and ferrocene moieties. When **1** is one-electron oxidized, the π–π^* transition band reduces and two broad bands at 1.5 and less than 0.6 eV appear below 2.0 eV. The absorption pattern is similar to those of one-electron-oxidized **2** and the sexithiophenes,[10] and further almost the same as for longer oligothiophenes (alkyl-duodecithiophene and alkyl-quindecithiophene).[10,11] On the other hand, the pattern is quite different from that of one-electron-oxidized ferrocenyl end-capped alkyl-sexithiophene that is considered to be attributable to LMCT. These results suggest that one-electron-oxidized species, such as a cation radical, is present in the methoxy-sexithiophene moiety of **1**.

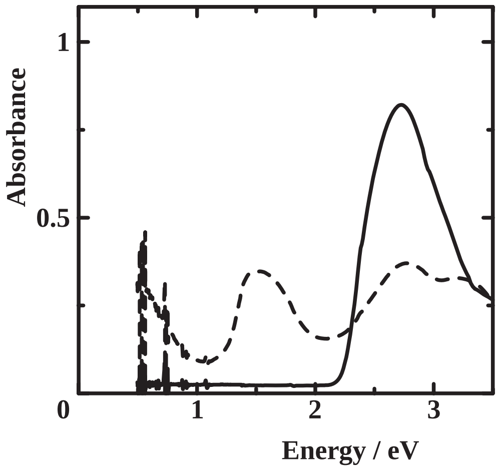

Figure 2. Electronic absorption specra of **1**: neutral one (solid line) and chemically one-elelctron-oxidized one (dashed line).

The electrochemical and optical data lead us to conclude the oxidized species produced in a ferrocene moiety strongly interacts with the methoxy-sexithiophene moiety and even with the other ferrocene moiety, in other word, a terminal interacts with the other terminal via the wire, the long sexithiophene moiety, in the oxidized state of **1**.

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