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Synthesis and electrochemical properties of ferrocene dimers and trimers bridged by an oligothiophene spacer*

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Abstract: We describe the design and synthesis of ferrocene dimers and trimers bridged by an oligothiophene spacer as both cathodic and anodic multiple redox-active organic–organometallic hybrid molecules. The electrochemical properties of all compounds were examined by cyclic voltammetry (CV). The voltammograms showed different multistep, multi-electron redox reactions derived from multi-ferrocene fragments and the organic spacer. The results indicate that a number of thiophene rings in the spacer can be attuned to the redox potentials and the electron-transfer processes.

Keywords: electrochemistry; electron transfer; ferrocene; mixed valency; oligothiophene; redox reaction.

INTRODUCTION

The study of ferrocene oligomers has attracted considerable current interest in organometallic chemistry due to their potential use as a good candidate for conductive materials, because the intra- and/or intermolecular electron transfer between Fe(II) and Fe(III) sites in the mixed-valence state derived from the partial oxidation of these multi-metallocene systems is expected to be capable of taking the place of attaining a semiconductivity through a hopping mechanism [1]. Moreover, multi-ferrocene compounds are fundamentally attractive target molecules for the study of the characteristic multi-electron transfer processes via a mixed valency [2]. In practice, multi-ferrocenes directly linked without a bridging unit, for example, the bi-, tri-, tetra-ferrocenes and their analogues, have been synthesized and their oxidation properties systematically evaluated [3].

For a decade, ferrocene dimers bridged by a π -conjugated spacer as one of the molecular wire models consisting of one organic spacer (π -electron system) and two organometallic redox-active terminals (ferrocene) have received much attention from the viewpoint of investigation of their electronic communication between the mixed-valency metal centers exhibiting charge delocalization depending on the electronic nature and length of the linking organic spacer. For example, diferrocenyl-oligoenes [4], diferrocenyl-oligoynes [5], diferrocenyl-cumulenes [6], diferrocenyl-oligoarenes [7], and others have been reported.

On the other hand, α -oligothiophenes with a π -conjugated system, which possess outstanding thermo- and photostabilities, geometric and electronic structures, and electronic and optical properties, have attracted much attention due to their potential use in next-generation electronic and optical devices [8]. In particular, it is well known that α -oligothiophene and its analogues are important organic semi-

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conducting materials for applications in electronic devices such as organic thin-field transistors (OTFTs) [8]. The electronic conductivity in α -oligothiophene depends on the redox ability (low ionization potentials) and charge delocalization along the α -oligothiophene backbone reflecting the electronic nature and π -conjugated planar structure of the oligomer of thiophene with the π -donor ability of the heterocycles having a heavy atom (sulfur). Their π -electron donor and charge delocalization ability is expected to enhance the electronic communication in a one-dimensional mixed-valence system consisting of two redox-active centers bridged by an α -oligothiophene spacer in comparison to the other π -conjugated spacer. Therefore, research into the synthesis and electronic properties of ferrocene dimers with π -conjugated thiophene spacers containing α -oligothiophene has been focused on investigating the charge transfer and delocalization (electronic communication between mixed-valency metal centers) in their mixed-valence system [9].

In this research field, our interest lies in the construction of new types of multi-electron transfer systems containing not only an oxidation process of two terminal ferrocene segments (organometallic redox-active center), but also oxidation and/or reduction processes of a π -conjugated thiophene segment (organic redox-active center) using a simple ferrocene dimer with a π -conjugated thiophene spacer. Based on our current results, we have already reported the synthesis and the electrochemical properties of 2,3-diferrocenylbenzo[b]- and 1,3-diferrocenylbenzo[c]-thiophenes regarded as a ferrocene dimer bridged by a benzannulated thiophene with an extended π -conjugation [10]. The redox behavior of the synthesized ferrocene dimers showed two well-defined reversible one-electron oxidation processes assigned to the stepwise formation of the di-(ferrocenium cation) via a mixed-valency and a one-step reversible reduction process assigned to the formation of the stable benzothiophene radical anion. Thus, we have succeeded in the development of a new donor-acceptor-type organic (thiophene)-organometal-lic (ferrocene) hybrid molecule with the potential of multi-electron transfer reactions derived from organic and organometallic redox fragments.

For the next step, we have designed two ferrocene dimers with α -bithiophene and α -terthiophene in order to develop new types of donor-acceptor-type organic (thiophene)-organometallic (ferrocene) hybrid molecules. With respect to the molecular design, we have studied the effect of the α -oligothiophene spacer with a different number of thiophene rings from the following two viewpoints of the redox reaction: (1) the redox reaction of the organic redox center affected by enhancement of the donor-acceptor ability based on extension of the π -conjugation length of the α -oligothiophene with the increasing number of thiophene rings, and (2) the oxidation reaction of two ferrocene units via mixed valency controlled by the strength of the electronic communication depending on the distance between the metal-metal centers determined by the number of thiophene rings (length of organic spacer).

On the other hand, although the synthesis and characterization of several ferrocene dimers with a π -conjugated thiophene spacer have been reported, there is no report concerning ferrocene trimers with two thiophene spacers, which involve a multi-step multi-electron transfer mechanism derived from their tri-metallocene system. Therefore, we have also designed 1,1'-bis{2-(5-ferrocenylthienyl)}- and 1,1'-bis{5-(5'-ferrocenyl-2,2'-bithienyl)}-ferrocenes as a ferrocene trimer with two thiophene or α -bithiophene spacers.

In this paper, we provide the details of the synthesis and electrochemical properties of a ferrocene dimer bridged by α -bithiophene or α -terthiophene spacers and a ferrocene trimer bridged by two thiophene or α -bithiophene spacers. In addition, we report the electrochemical properties including the known oxidation [7a,11] and unknown reduction process of 2,5-diferrocenylthiophene as a basic ferrocene dimer for comparison.

SYNTHESIS OF FERROCENE DIMERS AND TRIMERS BRIDGED BY AN OLIGOTHIOPHENE SPACER

2,5-Diferrocenylthiophene (1) as a basic thiophene-bridged ferrocene dimer was prepared via the Pd-catalyzed cross-coupling reaction of 2,5-dibromothiophene with ferrocenylzinc chloride in

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tetrahydrofuran (THF) under reflux conditions based on the previously reported methods [7a]. We achieved the synthesis of 5,5'-diferrocenyl-2,2'-bithiophene (2) and 5,5"-diferrocenyl-2,2':5',2"-terthiophene (3) through the same transition-metal-catalyzed cross-coupling reaction of the corresponding dibromo-derivatives with ferrocenylzinc chloride. These results are shown in Scheme 1.



Scheme 1 Synthesis of a series of ferrocene dimers.

1,1'-Bis(2-thienyl)- and 1,1'-bis{5-(2,2'-bithienyl)}-ferrocenes as a starting material due to the synthesis of a ferrocene trimer bridged by two thiophene or α -bithiophene fragments were prepared by the reported method [12]. The quantitative synthesis of 1,1'-bis-{2-(5-bromothienyl)}ferrocene was established by selective lithiation at the 5-positions of the two thiophene rings bridged by the ferrocene unit of 1,1'-bis-(2-thienyl)ferrocene with butyl lithium in THF at -50 °C, followed by bromination with 1,2-dibromo-1,1,2,2,-tetrafluoroethane. Introduction of two ferrocenyl groups, the synthesis of 1,1'-bis{2-(5-ferrocenylthienyl)}ferrocene with ferrocene with ferrocenyl groups, the synthesis of 1,1'-bis{2-(5-bromothienyl)}ferrocene with ferrocenylzinc chloride in the presence of a catalytic amount of bis(triphenylphophine)Pd(II) dichloride, (PPh₃)₂PdCl₂, under THF reflux condition in moderate yield. The synthesis of 1,1'-bis{5-(5'-ferrocenyl-2,2'-bithienyl)}ferrocene (**5**) was identically achieved through a two-step process from 1,1'-bis{5-(2,2'-bithienyl)}ferrocene involving the selective bromination at the α -positions of the outer two thiophene rings (the first-step reaction) and the introduction of two ferrocenyl groups using a Pd-catalyzed cross-coupling reaction (the second-step reaction) (Scheme 2).



Scheme 2 Synthesis of ferrocene trimers.

ELECTROCHEMICAL PROPERTIES OF FERROCENE DIMERS AND TRIMERS WITH AN OLIGOTHIOPHENE SPACER

The solution redox properties of ferrocene dimers 1-3 with oligothiophene spacers (thiophene, α -bithiophene, α -terthiophene) and ferrocene trimers 4, 5 with two thiophene or α -bithiophene spacers have been examined by electrochemical measurement (cyclic voltammetry, CV). The data are collected in Table 1 and the typical cyclic voltammograms (CVs) are shown in Figs. 1 and 2.

Compound	$E_{1/2} (-1/-2)^{\rm b}$	$E_{1/2} (0/-1)^{b}$	$E_{1/2} (0/+1)^{\rm c}$	$E_{1/2} (+1/+2)^{\rm c}$	$E_{1/2} (+2/+3)^{\rm c}$	$E_{1/2} (+3/+4)^{\rm c}$
Ferrocene di	mer					
1	_	-2.85	+0.23	+0.48	_	_
2	_	-2.50	+0.24	+.035	+1.44	_
3	-	-2.30		+0.28 (2e ⁻) ^d	+1.88	-
Ferrocene tri	mer					
4	-3.03 ^e	-2.79	+0.17	+0.33	+0.60	_
5	-2.57	-2.54	+0.19	+0.29	+0.41	+1.38

Table 1 Electrochemical data^a from CV for compounds 1-5.

^aAll the half-wave potentials [V] vs. Ag/Ag⁺ couple.

^bMeasured in 0.1 mol dm⁻³ [Bu₄N][PF₆]/THF solution; scan rate, 100 for **1**, **4** and 200 mVs⁻¹ for **2**, **3**, **5**; temperature, 248 for **1**, 233 for **2**, 293 for **3**, 243 for **4**, and 253 for **5**.

^cMeasured in 0.05 mol dm⁻³ [Bu₄N][B(C₆F₅)₄]/CH₂Cl₂ solution; scan rate, 100 for **4** and 200 mVs⁻¹ for **1–3**, **5**; temperature, 293 K.

^dTwo-electron one-step oxidation process, $E_{1/2}$ (0/+2) value provided.

eIrreversible reduction process, E_{pc} (-1/-2) value provided.

The CV of **1** measured in a concentration 1.0 mmol dm⁻³ sample in 0.05 mol dm⁻³ [Bu₄N]⁺[B(C₆F₅₎₄]⁻/CH₂Cl₂ solution showed two well-separated reversible one-electron oxidation waves. The first and second oxidations at half-wave potentials ($E_{1/2}$) of +0.23 and +0.48 V are assigned to stepwise formation of the diferrocenium cation state. The CV of **2** under the same condition showed two subsequent sets of oxidations with an electrochemical reversibility, $E_{1/2}$ (0/+1) = +0.24 V, $E_{1/2}$ (+1/+2) = +0.35 V, derived from the formation of the diferrocenium cation via a mixed-valence state in the anode scan from -0.3 to +0.7 V. The differences between the first and second oxidation half-wave potentials [$\Delta E_{1/2} = E_{1/2}$ (+1/+2) - $E_{1/2}$ (0/+1)] for the Fe(II)-Fe(III) and Fe(III)-Fe(III) couples of compounds **1** and **2** are +0.25 and +0.11 V, respectively. Based on these $\Delta E_{1/2}$ values, the comproportionation constants ($K_c = \exp[\Delta E_{1/2}F/RT$]) relative to the equilibrium

$$Fc-Th_n-Fc + Fc^+-Th_n-Fc^+ \leq 2 Fc^+-Th_n-Fc$$

were calculated to be 2.0×10^4 for 1 and 7.8×10 for 2 for each mixed-valence state. The extremely large K_c value of 1 compared with that of 2 suggests the presence of stabilization of the mixed-valence intermediate contributing to strong electronic communication (based on charge delocalization) between ferrocene and the ferrocenium cation along the thiophene spacer in the mixed-valence state. On the other hand, in the anode scanning of 3 range from -0.3 to +0.6 V under the same condition, a twoelectron one-step reversible oxidation process assigned to the synchronous oxidation of the two terminal ferrocenyl groups at the same potentials was observed, reflecting the absence of electronic interaction between Fe(II) and Fe(III) centers in the mixed-valence state. The observed oxidation behavior of ferrocene dimers 1–3 demonstrates that the electronic communication in the mixed-valence state depends upon the distance between the ferrocene metal centers determined by the number of thiophene rings (length of organic spacer).

On the other hand, the oxidation process of 5,5"-diferrocenyl-3,3'-dimethoxy-2,2':5',2"terthiophene as a similar ferrocene dimer system has been reported to show double redox waves with

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Fig. 1 CVs (cathodic scan, left; anodic scan, right) of ferrocene dimers 1 (upper), 2 (middle), and 3 (bottom).

 $\Delta E_{1/2} = +0.13$ V corresponding to a two-step two-electron oxidation derived from the two terminal ferrocenyl groups, reflecting the presence of strong electronic communication between the metal centers in the mixed-valence state [9b]. This notable difference suggests that the electron-donating effect of the methoxy group on the terthiophene spacer enhances electronic communication between the mixed-valence metal centers. Therefore, the important factor contributing to efficient electronic communication between the ferrocene fragments and the π -electron density of the π -conjugated organic spacer linking the ferrocene fragments.

By anode scanning of compounds 2 and 3 to +1.5 V, the third reversible oxidation waves assigned to the one-electron oxidation of the organic redox center (oligothiophene moiety) after the formation of a di-(ferrocenium cation) are observed at +1.44 and +1.18 V, respectively. The cathode shift of the third oxidation potential $[E_{1/2} (+2/+3)]$ of compound 3 in comparison with that of 2 suggests that the donor ability of the organic redox center increases with elongation of the effective π -conjugation length from α -bithiophene to α -terthiophene. In the case of compound 1, the corresponding oxidation of the thiophene center could not be observed in an anodic potential window, because it has essentially a high oxidation potential of the formation of the multiply charged oxidation species containing the di-(ferrocenium cation) and the thiophene radical cation due to the strong coulombic (electrostatic) repulsion.

On the negative scan, the CV of three kinds of ferrocene dimers 1-3 in a concentration 1.0 mmol dm⁻³ sample in 0.1 mol dm⁻³ [Bu₄N]+[PF₆]⁻/THF solution showed reversible one-electron reduction

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Fig. 2 CVs (cathodic scan, left; anodic scan, right) of ferrocene trimers 4 (upper) and 5 (bottom).

couples; $E_{1/2}$ (0/–1) = –2.85 V for 1, –2.50 V for 2, –2.30 V for 3, derived from the formation of the radical anion species. The tendency of the anode shift of the reduction half-wave potentials [$E_{1/2}$ (0/–1)] clearly indicates that the extension of the π -conjugation lengths within the bridging oligothiophene spacer with the increasing number of thiophene rings from 1 to 3 leads to the enhancement of acceptor ability attributed to the lowest unoccupied molecular orbital (LUMO) energy level in the order of 3 > 2 > 1.

The CV scans of ferrocene trimers **4** and **5** containing three ferrocene units and two thiophene or α -bithiophene spacers in a concentration 1.0 mmol dm⁻³ sample in 0.05 mol dm⁻³ [Bu₄N]⁺[B(C₆F₅)₄]⁻/CH₂Cl₂ solution showed three electrochemically reversible one-electron redox couples with three half-wave potentials of +0.17, +0.33, and +0.60 V for **4**, +0.19, +0.29, and +0.41 V for **5** via two kinds of mixed-valency corresponding to two equivalent outer ferrocene units and the unequivalent central ferrocene unit in these molecules. The two K_c values were calculated to be 5.7×10^2 and 4.4×10^4 for **4**, and 5.2×10 and 1.6×10^2 for **5** from two $\Delta E_{1/2}$ values for the mono-and di-(ferrocenium cation) couple and the di- and tri-(ferrocenium cation) couple according to the following two equilibria:

$$\begin{split} [\text{Fc}-\text{Th}_n-\text{Fc}-\text{Th}_n-\text{Fc}] + [\text{Fc}-\text{Th}_n-\text{Fc}-\text{Th}_n-\text{Fc}]^2 + & \leftrightarrows 2 \ [\text{Fc}-\text{Th}_n-\text{Fc}-\text{Th}_n-\text{Fc}]^+ \\ [\text{Fc}-\text{Th}_n-\text{Fc}-\text{Th}_n-\text{Fc}]^+ + [\text{Fc}-\text{Th}_n-\text{Fc}-\text{Th}_n-\text{Fc}]^3 + & \backsim 2 \ [\text{Fc}-\text{Th}_n-\text{Fc}-\text{Th}_n-\text{Fc}]^2 + \end{split}$$

All K_c values are considerably larger than the statistical limit of 4.0 calculated from the $\Delta E_{1/2}$ values of approximately 36 mV expected at 20 °C for two non-interacting redox centers [2,4]. These results clearly indicate that all the mixed-valence intermediates produced by one- or two-electron oxidations are stabilized by electronic communication between the three metal centers through two thiophene or α -bithiophene spacers in these ferrocene trimer systems. In addition, the degree of electronic communication in the mixed-valence state depends upon the distance between each of the metal centers

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determined by the length of the organic spacer linking three ferrocene units. In the anode scan of **5** in an anodic potential window under the same condition, a further one-electron oxidation wave assigned to the oxidation of one of the two α -bithiophene fragments followed by the formation of a tri-(ferrocenium cation) was observed, $E_{1/2}$ (+3/+4) = +1.38 V, but no oxidation of another α -bithiophene fragment could be observed. In the case of compound **4**, oxidation of two thiophene fragments on the tri-(ferrocenium cation) intermediate (a three-electron oxidant) could not be observed in a limited anodic potential range. The difference in the oxidation process is caused by increasing donor ability with increasing π -conjugation length and decreasing coulombic (electrostatic) repulsion between the positive by charged ferrocenium cations with increasing metal–metal distance.

On the negative scan, the CV of **4** and **5** for a concentration 1.0 mmol dm⁻³ sample in 0.1 mol dm⁻³ [Bu₄N]⁺[PF₆]⁻/THF solution showed two subsequent one-electron reduction processes. The first reduction is assigned to formation of a radical anion derived from the one-electron reduction of one of the two organic redox centers, and the following second reduction is assigned to the formation of dianion diradical species containing two radical anion segments separated from each other by a bridging central ferrocene unit. The reversible first and irreversible (involving decomposition) second reduction peaks were observed in the CV of **4**, $E_{1/2}$ (0/–1) = –2.79 V; E_{pc} (–1/–2) = –3.03 V. On the other hand, the two reduction waves of **5** were observed as electrochemical reversibility reflected in the stable generation of the dianion diradical species, $E_{1/2}$ (0/–1) = –2.54 V; $E_{1/2}$ (–1/–2) = –2.57 V. This observation suggests that the effect of extended π -conjugation of the α -bithiophene skeleton influences the two-step, two-electron reduction process of the ferrocene trimer with two α -bithiophene spacers due to increasing the electron-accepting ability (anodic reduction potential) and the stability of mono- or di-(radical anion) species generated by one- or two-electron reduction reactions contributing to the spin delocalization (enhancement of electrochemical reversibility).

The results of the CV measurements demonstrate the outstanding multi-electron transfer abilities of ferrocene trimers with two redox-active organic spacers as novel donor–acceptor-type organic–organometallic hybrid redox-active molecules. In particular, it should be noted that the redox behavior of the ferrocene trimer bridged by two α -bithiophene spacers remarkably showed the multiple electron-transfer processes with a five-site, six-electron, six-step reversible redox reaction containing a three-step, three-electron oxidation derived from three ferrocene fragments via two kinds of mixed-valency and a further one-electron oxidation derived from one of the α -bithiophene fragments (a total four-electron oxidation process in the anodic scan), and a two-step, two-electron reduction derived from two equivalent α -bithiophene segments assigned to the stepwise formation of di-(radical anion) species (two-electron reduction process in the cathodic scan).

CONCLUSION

In conclusion, we have designed and synthesized a series of novel ferrocene dimers 2, 3 with oligothiophene spacers (α -bithiophene, α -terthiophene) and ferrocene trimers 4, 5 with two thiophene or α -bithiophene spacers. The electrochemical properties of these compounds were identified by a CV technique. 2,5-Diferrocenylthiophene (1) as a basic ferrocene dimer for comparison has been synthesized and its electrochemical properties evaluated, including its known oxidation and unknown reduction processes. These multi-ferrocene compounds with thiophene or α -oligothiophene spacers showed different electrochemical responses, which have redox potentials and a multi-electron transfer process controlled by the π -conjugation effect and the length of the organic spacer attuned to the number of thiophene rings. In particular, the results of the redox behavior of ferrocene trimers 4, 5 could be described as a new type of one-dimensional molecular wire model consisting of three metallocenes and two π -conjugated spacers for the first time in organometallic chemistry. Based on the results of the CV measurements, we have succeeded in establishing new types of organic (thiophene)-organometallic (ferrocene) hybrid molecules possessing both anodic and cathodic reversible multi-electron transfer

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abilities. Above all, the α -bithiophene bridging ferrocene trimer **5** remarkably exhibits multiple electron-transfer processes with a five-site, six-electron, six-step reversible redox reaction, which has never been achieved, and thus is expected as a potentially important candidate for applications as conducting materials. This study opens further possibilities to control the electronic communication in the mixed-valence system derived from multi-metallocenes by fully exploiting the investigation of both ferrocene dimers and trimers bridged by an oligothiophene spacer.

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