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Synthesis and properties of 1,1'-bis(diacetylene-group) connected ferrocene-thiophene derivative: a cooperatively functional behavior of diacetylene-group connected constituents

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Introduction

Transformable π -electronic molecular systems between the well-defined conformations (conformers) are fascinating in not only structural changes but also spectral changes, and thus of great significance especially in the field of functional materials science. For example, the dimers of octaethylporphyrin(M) [OEP(M)] connected with the ethylene linkage are well known to transform their geometry between anti- and syn-conformations depending on the coordinated metals of OEP(M) (Chart 1).¹ The OEP(Zn) dimer exists in syn-conformation preferably like a tweezers structure due to greater dipole-dipole interaction between polarized OEP(Zn) rings, in contrast with anti-conformation of the corresponding OEP(Ni) dimer, exhibiting the split circular dichroic (CD) spectrum induction as a chiral host molecule.² However, in case of the related ethylene-group connected OEP(Ni) tetramers, as contrasted with anticonformation of the derivative 1 similar to OEP(Ni) dimer, the derivative 2 unexpectedly exists in syn-conformation predominantly to show a chirogenic function similar to OEP(Zn) dimer.³ This result conclusively indicates that the diacetylene linkage plays an important role not only for extension of π -electronic conjugation but also for van der Waals interaction between the two highly extended OEP(Ni) constituents in 2 to compensate their steric repulsion sufficiently (Chart 1).4

ABSTRACT

An extended π -electronic conjugation system of 1,1'-bis(diacetylene-group) connected ferrocene-thiophene derivative has been synthesized, with our integrated reaction between the corresponding TMSprotected acetylenes in one-pot. Its electronic properties have been examined, suggesting a cooperatively functional behavior of the diacetylene-group connected constituents.

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On one hand, in recent years, a great deal of effort has been paid for materials science based on the ferrocene nucleus [Fc: Cp₂Fe(II)],⁵ by virtue of its transformable functionality in axis-rotation similar to the ethylene linkage.⁶ However, systematic study on the structure-property relationship of the Fc derivatives extended with such multi-functional diacetylene linkage has scarcely been made until guite recently, especially from the viewpoint of materials science.⁷ On the basis of those simple and well-defined transformable conformers, useful findings for the new functional Fc molecules could be derived from the analysis and evaluation of their properties, in terms of not only one-dimensional interaction between π -electron rich Cp ring and π -electronic system (π ES) through the diacetylene linkage but also spatial interaction between two highly extended $Cp-\pi ES$ conjugation constituents (Chart 2). In particular, as the two extended Cp- π ES conjugation constituents rotate round the Fc axis freely, molecular functions would be brought purposively from the spectral changes by both the control of molecular motion and the manipulation of various spatial interactions between them. In this respect, the hetero-aryl ring is a typical candidate as πES for this purpose, because it possesses not only the mobile π -electrons but also the lone-pair electrons on heteroatoms, which would respond susceptibly to various outside stimulations such as electrochemical action and metal coordination, further than the hydrocarbon-aryl ring. As the first example along this line, the Fc derivative 3 was designed, in which Cp and thiophene (Th) rings attached at each end of the diacetylene linkage are cooperative in the π -electronic conjugation and yet the

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Chart 2

Cp-Th conjugation constituents in **3** spatially interact with each other under the particular conditions (Charts 2 and 3).

In this letter, the synthesis, electronic, and electrochemical properties of **3** will be reported together with a brief demonstration on its metal-sensing behavior, as compared with those of the related compounds **4**, **5**, and **6** (Chart 3).

The Fc-Th and Fc-Th₂ derivatives **3** and **4** were synthesized, as shown in Schemes 1 and 2. As usual, the oxidative coupling between terminal acetylenes of Fc (**7**,⁸ 1 equiv) and Th (**8**,⁹ 1.1 equiv) under the Eglinton-coupling conditions¹⁰ afforded the diacetylenegroup connected Fc-Th derivative **4**,¹¹ Fc-dimer **5**,¹¹ and Th-dimer **6**¹¹ in 85%, 5%, and 3% yields, respectively. On the other hand, the 1,1'-bis(diacetylene-group) connected Fc-Th₂ derivative **3** can not



be obtained under the same reaction conditions as above, because the 1,1'-diethynyl Fc derivative corresponding to 7 is extremely unstable to be employed in synthetic reactions.¹² Then, according to a general synthetic method for 1,1'-bis(diacetylene-group) connected Fc derivatives, just recently developed by us,13 one-pot reaction between trimethylsilyl (TMS)-protected Fc derivative 9 and 2-ethynyl Th derivative 8 under the TMS-deprotection and Eglinton-coupling conditions was applied to the synthesis of 3. As expected, the desired compound $\hat{\mathbf{3}}^{\hat{1}1}$ could be obtained as a stable compound. But, its yield was 20% at most with low reproducibility. Under the present reaction conditions, Th-dimer 6 formed in large quantity together with insoluble Fc polymer, indicating the much higher reactivity of the Th terminal acetylene 8 toward oxidative homo-coupling than the hydrocarbon-aryl terminal acetylene.^{13b} Therefore, taking the fact into consideration, the coupling reaction between both TMS-protected reactants 9 and 10 was carried out under the similar conditions, consequently affording **3** in a fairly good yield of 77%. Dimethoxyethane (DME) as a co-solvent was also found to work effectively for the present tandem reactions, prior to CHCl₃.¹³ This is the first synthetic example where the hetero-aryl ring is incorporated into the Fc- $(\pi ES)_2$ system.

The structures of **3**–**6** were determined by Mass, IR, ¹H NMR, and UV–vis spectral measurements, as well as elemental analyses. In ¹H NMR spectra of **5** and **6**, it is shown that the diacetylene linkage induces low-field shift of Th-protons (Th-H) by 0.05–0.15 from the corresponding ones of Th (δ = 7.04 and 7.19 ppm) and of Cp-H by 0.1–0.4 ppm from those of Fc (δ = 4.15 ppm), respectively. In case of the Fc-Th and Fc-Th₂ derivatives, Cp-H of **3** appeared at the lower field than those of **4**. The former can be explained by both





Figure 1. Electronic absorption spectra of 3 (red), 4 (purple), 5 (blue), and 6 (yellow) in CHCl₃ solution (1.1–1.3 \times 10⁻⁵ mol cm⁻³).

inductive effect and anisotropic effect of the diacetylene linkage in consequence. On the other hand, the latter could be attributed to anisotropic effect of the increased diamagnetic ring current of the Cp ring by connection with diacetylene linkage. Otherwise, it suggests greater significance of syn or synclinal conformation in **3** due to an attractive interaction between the two Cp-Th extended conjugation constituents, where another small anisotropic effect has influence on the opposite Th-H mutually more or less (Chart 2).

The electronic absorption spectra of 3-6 in CHCl₃ are shown in Figure 1. As is generally observed in Fc nuclei,¹⁴ the Fc derivatives 3, 4, and 5 characteristically exhibit very broad and weak bands at 400-550 nm due to the 3d-3d transition in Fe(II). In contrast with several vibration bands (λ_{max} = 265, 292, 347, and 365 nm) of Thdimer 6, the main band of Fc-dimer 5 shows almost one broad band at λ_{max} = 290 nm, indicating that the electronic structure $(\lambda_{\text{max}} = 235 \text{ nm})^{15}$ of Th is much more perturbed by the diacetylene $(\lambda_{\text{max}} = 255 \text{ mm})^{-10}$ of first model more percented by 14 of Fc. It simply linkage as compared with that $(\lambda_{\text{max}} = 276 \text{ nm})^{14}$ of Fc. It simply concludes that the energy levels of HOMO and LUMO of the diacetylene linkage are much closer to those of Th ring to interact with each other efficiently. On the other hand, the derivatives 3 and 4 exhibited the electronic nature of both Fc and Th rings, implying an electronic interaction between them through the diacetylene linkage. In particular, on the basis of **4**, the Fc-Th₂ derivative **3** afforded a further combined spectrum between those of 5 and 6, showing a fairly increased intensity in the main band and a small



Figure 2. Cyclic voltammograms of **3** (red), **4** (blue), and **5** (black) in CH₂Cl₂ solution (ca. 6.5×10^{-4} mol cm⁻³). Electrodes: GC (working), Pt (counter), and SCE (reference). Supporting electrolyte: 0.1 M *n*-Bu₄NClO₄, scan rate: 120 mV/s. Electrochemical reactions were carried out within range between 1.30 V and -0.3 V. Because of no I_p waves, lines below 0.0 V were cut off for simplification.

bathochromic shift ($\Delta\lambda$ =12 nm) in the 3d–3d transition band.¹¹ These results conclude that the diacetylene linkage plays an important role as a transmission mediator to make an electronic communication between Cp and Th rings smoothly (vide infra), though further theoretical studies are necessary for clarification of these absorption band origins.

As a measure of electron-releasing behavior (Fc^{2+}/Fc^{3+}) , the oxidation potentials of Fc derivatives 3, 4, and 5 were examined in CH₂Cl₂, under the conditions where the half-wave oxidation potential $(E_{1/2}^{0x})$ of Fc shows 0.53 V versus SCE in a reversible redox system.¹⁶ Similar to Fc, all the derivatives 3-5 exhibited a reversible redox wave (Fig. 2). Depending on the number of Fc nucleus, Fc-dimer 5 was oxidized via two one-electron transfer processes affording the voltammogram with a shoulder wave at a scan rate of 120 mV/s, while both Fc derivatives 3 and 4 simply afforded the single-step voltammogram under the same conditions. As compared with Fc, the derivatives **5** ($E_{1/2(1)}^{\text{ox}} = 0.61$ and $E_{1/2(2)}^{\text{ox}} = 0.72$ V), **4** ($E_{1/2}^{\text{ox}} = 0.66$ V), and **3** ($E_{1/2}^{\text{ox}} = 0.80$ V) were found to resist electrochemical oxidation in order, clearly indicating that the diacetylene linkage stabilizes their first electron-releasing energy level efficiently. Among them, the stabilization difference of **3** was outstanding, distinct from Fc, even as compared with 4. Firstly, this result indicates that an inductive effect of the Th-diacetylene components reduces the electron density of Cp ring to lower the electron-donativity from Cp to Fe(II) and thus the barer Fe(II) ion results in weakening the electron-releasing ability. In other words, the Cp ring likely gains more resonance energy as



Figure 3. Electronic absorption spectral changes by adding 0.0 equiv (red), 10 equiv (purple), and 50 equiv (blue) of AgNO₃ into AN solution (ca. 1.1×10^{-5} mol dm⁻³) of (right) **3** and (left) **4**.

 6π -electron cyclic system, as also mentioned in ¹H NMR spectral results. Secondly, besides such a strengthened aromaticity of the Cp ring in **3**, a possibility of the spatial interaction between the Cp-Th conjugation constituents in syn or synclinal conformation with more significance in **3** might not still be abandoned (Chart 2), although the clarification on the electrochemical stabilization of **3** should wait for further experimental study.¹¹

In connection with highly electron-donor ability of the Fc derivatives, the affinity behavior of **3** and **4** for several transition-metal ions were preliminarily examined,¹⁷ by means of electronic absorption spectral measurement in acetonitrile (AN). Among them, the Fc-Th₂ derivative **3** was particularly sensitive to Ag⁺ ion to afford a new absorption band at 500-800 nm, probably due to MLCT transition band,¹⁸ while the Fc-Th derivative **4** showed no particular spectral change under the same conditions (Fig. 3). Supposing the complexation with Ag⁺ ion took place intermolecularly, the Fc-Th 4 should also exhibit the MLCT transition band similar to the Fc- Th_2 3 to some extent even under the applied conditions. Taking the structural difference between 3 and 4 into consideration, this result suggests that the Th-diacetylene conjugation constituents in **3** work cooperatively for an intramolecular complexation with Ag⁺ ion somehow. At present, it is premature to deduce the coordination sites for complexation between Th-diacetylene constituent and Ag⁺ ion. However, the two diacetylene-groups connected Cp-Th constituents likely face each other to associate with Ag⁺ ion like a tweezers structure in a syn or synclinal conformation (Chart 2).

In conclusion, the 1,1'-bis(diacetylene-group) connected Fc-Th₂ derivative **3** has been synthesized in high yield under the improved cross-coupling conditions between TMS-protected acetylenes **9** and **10**. ¹H NMR and UV-vis spectra and oxidation potential of **3** indicated that the diacetylene linkage works as a mediator for communication with Th and Cp rings smoothly, induces Cp ring to reduce its electron-density efficiently, and stabilizes Fc electrochemically. It is also suggested that the diacetylene-group connected Cp-Th constituents in **3** play a cooperative role for an intramolecular complexation with Ag⁺ ion. Further study on the synthesis and properties of 1,1'-bis(diacetylene-group) connected Fc derivatives carrying much larger sized π ES like OEP(M) is now in progress.¹⁷

Acknowledgments

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