



Synthesis and redox behavior of ene–diyne scaffolds that bear ferrocenes at the periphery

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ABSTRACT

The ene–diyne systems **1** and **2** possessing ferrocenyl groups at the periphery were prepared by the simple one-pot Sonogashira–Hagihara coupling reaction of ethynylferrocene (**3**) with 9-dibromomethylene-9H-fluorene (**4**) and 9,10-bis(dibromomethylene)-9,10-dihydroanthracene (**5**). The novel ferrocene-substituted ene–diyne compounds exhibited amphoteric redox behavior with a reversible one-stage electrochemical oxidation upon cyclic voltammetry.

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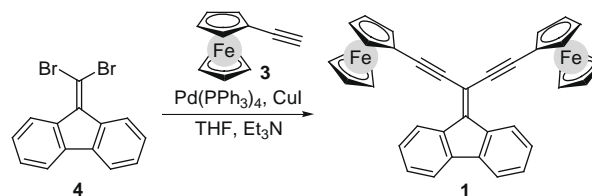
The ene–diyne unit is a molecular scaffold designed for molecular architectures that contain one- and two-dimensional carbon networks.¹ Interest in conjugated ene–dienes has grown because of their wide range of applications, for example in molecular wires, non-linear optics (NLOs), and molecular switches. Therefore, a variety of ene–diyne compounds have been prepared and their properties, for example, reactivity² and fluorescence properties³ have been examined. Recently, we have also reported the synthesis of two types of ene–diyne systems utilizing methylene-9H-fluorene and anthraquinodimethane as platforms for redox-active substructures that bear 6-azulenyl groups at the periphery. The anthraquinodimethane derivatives exhibit two one-step two-electron redox reactions with significant color change under electrochemical reduction conditions.⁴

Ferrocene has attracted the interest due to its redox properties with a lower oxidation potential to form a stabilized radical cation (ferricinium ion). Thus, a large number of the compounds bearing ferrocenyl groups have been synthesized and their properties including intramolecular interactions with the ferrocenyl groups have been extensively studied.⁵ Recently, preparation of ene–diyne compounds bearing ferrocenyl group has been reported by several groups.⁶ Ogawa et al. also reported the synthesis of novel benzochalcogenophenes containing ferrocenyl units, which exhibited reversible redox behavior attribute to the generation of stable radical anion and cation in CV.⁷ However, preparation and properties of ferrocene-substituted ene–diyne compounds binding with π -electron core have never been reported. The ene–diyne compounds with multiple ferrocenyl moieties are expected to show novel multi-electronic redox properties. Herein, we report the synthesis of ene–diyne compounds **1** and **2** that bear ferrocenyl groups at the

periphery to examine their redox behavior and intramolecular interaction between the ene–diyne cores with ferrocenyl groups at the periphery.

Compounds **1** and **2** were prepared by Pd-catalyzed alkynylation of ethynylferrocene (**3**) with 9-dibromomethylene-9H-fluorene (**4**)⁸ and 9,10-bis(dibromomethylene)-9,10-dihydroanthracene (**5**)⁹, under Sonogashira–Hagihara conditions.¹⁰ The cross-coupling reaction of **3** with the 9H-fluorene derivative **4** using Pd(PPh₃)₄ as a catalyst, and subsequent chromatographic purification of the reaction mixture on silica gel, afforded the desired ene–diyne **1** in 83% yield (Scheme 1).¹¹ Likewise, the reaction of **3** with **5** afforded **2** in 71% yield (Scheme 2).¹² These new compounds **1** and **2** are stable, reddish-brown colored crystals and can be stored in the crystalline state at room temperature.

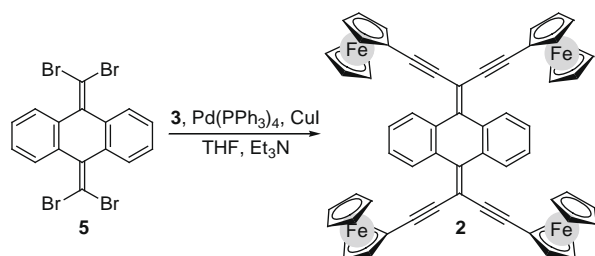
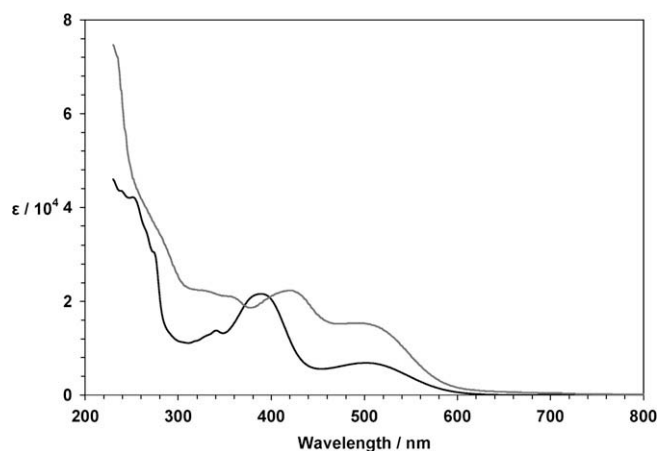
Compounds **1** and **2** were fully characterized by their spectroscopic data (see Ref. 11,12). The mass spectra of **1** and **2** ionized by ESI showed their correct molecular ion peaks. The characteristic stretching vibration band of the ethynyl groups in **1** and **2** was observed at $\nu = 2187\text{ cm}^{-1}$ and 2189 cm^{-1} , respectively, in their IR spectra. These results are consistent with the structure of these products. UV–vis spectra of **1** and **2** showed characteristic absorption bands arising from the ferrocene moieties in visible region as shown in Figure 1. UV–vis spectra of **1** showed characteristic



Scheme 1. Synthesis of **1**.

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Scheme 2. Synthesis of **2**.Figure 1. UV-vis spectra of **1** (black line) and **2** (gray line) in dichloromethane.

absorption bands attributable to both ferrocenyl (λ_{\max} ($\log \epsilon$) = 505 nm (3.83)) and 9H-fluorenylidene (λ_{\max} ($\log \epsilon$) = 390 nm (4.33)) moieties. The longest wavelength absorption band of **1** showed a bathochromic shift compared with that of parent ferrocene, probably due to the expansion of the π -conjugation by the ethynyl substituent. Compound **2** also represented the characteristic absorption bands responsible for its reddish-brown color at similar wavelength region (λ_{\max} ($\log \epsilon$) = 500 nm (4.18)). The extinction coefficients increased with the number of ferrocene rings substituted.

To clarify the electrochemical properties, the redox behavior of **1** and **2** was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Measurements were carried out with a standard three-electrode configuration. Tetraethylammonium perchlorate (0.1 M) in benzonitrile was used as a supporting electrolyte with platinum wire auxiliary and working electrodes. All measurements were carried out under an argon atmosphere, and potentials were related to an Ag/AgNO₃ reference electrode and Fc/Fc⁺ as an internal reference, which discharges at +0.15 V under these conditions. The redox potentials (in volts vs Ag/AgNO₃) of **1** and **2** are summarized in Table 1.

Table 1
Redox potentials of **1** and **2**

Compound		E_{red}^1 (V)	E_{red}^2 (V)	E_{ox}^1 (V)
1	CV	−1.72		+0.32
	DPV	(−1.70)	(−1.90)	(+0.30)
2	CV			+0.31
	DPV	(−1.64)	(−2.05)	(+0.30)

Redox potentials were measured by CV and DPV [V vs Ag/AgNO₃, 1 mM in benzonitrile containing Et₄NClO₄ (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mV s^{−1}, and Fc/Fc⁺ = +0.15 V]. In the case of reversible waves, redox potentials measured by CV are presented. The peak potentials measured by DPV are shown in parentheses.

^{1,2} First and second reduction potential.

Amphoteric redox behavior of compounds **1** and **2** was revealed by CV and DPV. Electrochemical reduction of **1** showed a reversible reduction wave at half-wave potentials of −1.72 V in CV (Fig. 2), which can be attributed to formation of radical anion on 9H-fluorenylidene moiety. Reversible one-stage oxidation wave was also observed at +0.32 V in CV, which attributes to electrochemical oxidation of the two-ferrocenyl moieties of **1** to form dicationic species. Thus, the electrochemical behavior of **1** could be explained as shown in Scheme 3.

Compound **2** exhibited a reversible one-stage oxidation wave at +0.31 V in CV, which is attributed to the formation of tetracationic species derived from the electrochemical oxidation of the four-ferrocenyl groups of **2**. The electrochemical reduction also exhibited irreversible waves at −1.64 V and −2.05 V in DPV, probably due to the reduction of the dihydroanthracene moiety of the compound.

The oxidation potential of compounds **1** and **2** (**1**: +0.32 V and **2**: +0.31 V) is more positive compared with that of parent ferrocene (+0.15 V), which indicates less π -donating property and low HOMO level of ene-diyne compounds **1** and **2** compared with those of parent ferrocene. Despite the fact that **1** and **2** contain multiple ferrocenyl groups, cyclic voltammogram displays only a single anodic process with features of chemical reversibility. Moreover, the first oxidation potential of **1** is similar to that of **2**. These results reflect the lower electrochemical interaction among the ferrocenyl groups through the π -electron core.

In conclusion, ene-diyne compounds possessing the ferrocene on the terminal acetylenes **1** and **2** were prepared by the simple palladium-catalyzed alkylation of ethynylferrocene (**3**) with 9-

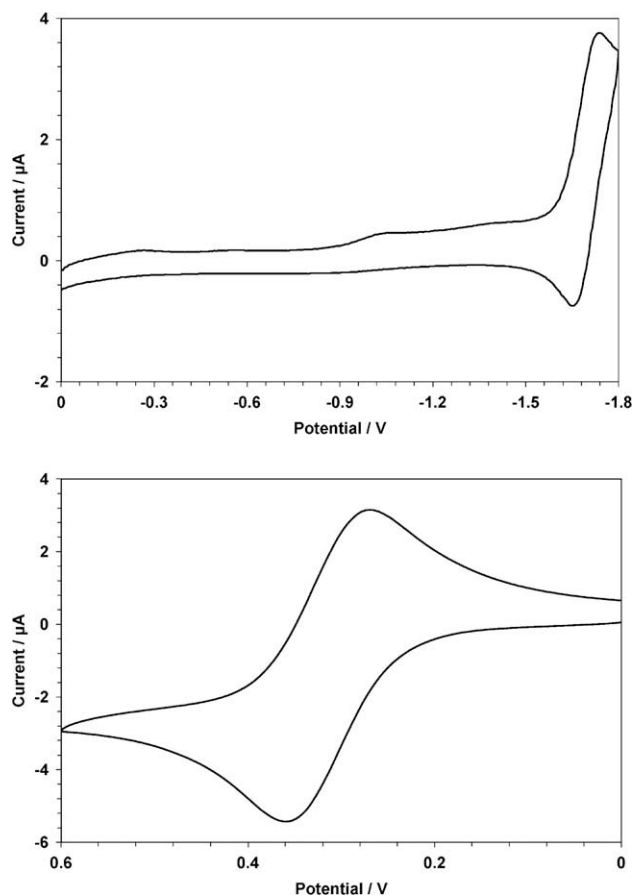
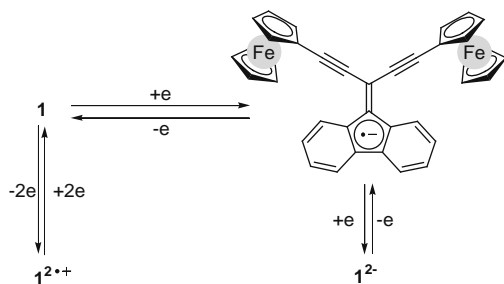


Figure 2. Cyclic voltammograms of the reduction and oxidation of **1** (1 mM) in benzonitrile containing Et₄NClO₄ (0.1 M) as a supporting electrolyte; scan rate = 100 mV s^{−1}.



Scheme 3. Presumed redox behavior of **1**.

dibromomethylene-9H-fluorene (**4**) and 9,10-bis(dibromomethylene)-9,10-dihydroanthracene (**5**) under Sonogashira–Hagihara conditions. Analysis by CV and DPV showed that compounds **1** and **2** exhibited a reversible one-stage oxidation wave, although **1** and **2** contain multiple ferrocenyl groups in their structures. Construction of reversible multi-stage redox systems utilizing the ene-diyne scaffolds is currently examined in our laboratory.

Acknowledgments

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- Synthesis of 1**: To a degassed solution of **3** (250 mg, 1.20 mmol), **4** (185 mg, 0.55 mmol), and CuI (19 mg, 0.10 mmol) in triethylamine (5 mL) and THF (5 mL) was added tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.05 mmol). The resulting mixture was stirred at 50 °C for 17 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with toluene. The organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give **1** (271 mg, 83%). Mp 196.0–198.0 °C (AcOEt); HRMS (ESI) calcd for [C₃₈H₂₆Fe₂ + Na]⁺: 617.0631, found: 617.0626; IR (KBr disk): ν_{max} = 3087 (w), 3072 (w), 3055 (w), 2187 (m), 1600 (w), 1560 (w), 1444 (m), 1431 (m), 1409 (w), 1352 (w), 1290 (w), 1145 (w), 1105 (m), 1053 (w), 1026 (m), 1001 (m), 956 (m), 945 (w), 927 (w), 817 (s), 781 (m), 732 (s), 690 (w), 640 (w), 630 (w), 528 (m), 503 (m), 482 (s), 451 (m), and 422 (w) cm⁻¹; UV-vis (CH₂Cl₂): λ_{max} (log ε) = 253 (4.62), 274 (4.48), 342 (4.13), 390 (4.33), and 505 (3.83) nm; ¹H NMR (400 MHz, CDCl₃) δ = 8.77 (dd, J = 6.8, 2.0 Hz, 2H, H-1',8'), 8.70 (d, J = 6.8, 2.0 Hz, 2H, H-4',5'), 7.42–7.35 (m, 4H, H-2',3',6',7'), 4.65 (dd, J = 2.0, 2.0 Hz, 4H, H-2.5 of Fc), 4.35 (dd, J = 2.0, 2.0 Hz, 4H, H-3,4 of Fc), and 4.32 (s, 10H, H-Cp); ¹³C NMR (100 MHz, CDCl₃) δ = 142.66, 139.70, 137.80, 128.92, 127.12, 124.78, 119.57, 102.78, 98.24, 85.84, 71.66, 70.20, 69.56, and 64.50. Anal. Calcd for C₃₈H₂₆Fe₂·1/2H₂O: C, 75.65; H, 4.51. Found: C, 75.72; H, 4.58.
- Synthesis of 2**: To a degassed solution of **3** (250 mg, 1.20 mmol), **5** (130 mg, 0.25 mmol), and CuI (19 mg, 0.10 mmol) in triethylamine (5 mL) and THF (5 mL) was added tetrakis(triphenylphosphine)palladium(0) (58 mg, 0.05 mmol). The resulting mixture was stirred at 50 °C for 24 h under an Ar atmosphere. The reaction mixture was poured into a 10% NH₄Cl solution and extracted with toluene. The organic layer was washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with CH₂Cl₂ to give **2** (184 mg, 83%). Mp >300 °C (AcOEt); HRMS (ESI) calcd for [C₆₄H₄₄Fe₄ + Na]⁺: 1059.0738, found: 1059.0733; IR (KBr disk): ν_{max} = 3091 (w), 2189 (m), 1637 (m), 1542 (m), 1450 (w), 1411 (w), 1377 (w), 1328 (w), 1290 (w), 1263 (m), 1201 (w), 1105 (m), 1043 (w), 1026 (m), 1001 (m), 960 (w), 821 (s), 771 (s), 680 (w), 624 (w), 524 (m), 486 (s), and 447 (s) cm⁻¹; UV-vis (CH₂Cl₂): λ_{max} (log ε) = 277 sh (4.55), 336 sh (4.34), 362 (4.31), 426 (4.34), and 500 (4.18); ¹H NMR (400 MHz, CDCl₃) δ = 8.42 (dd, J = 6.8, 2.0 Hz, 4H, H-1',4',5',8'), 7.44 (dd, J = 6.8, 2.0 Hz, 4H, H-2',3',6',7'), 4.50 (br s, 8H, H-2,5 of Fc), 4.21 (s, 10H, H-3,4 of Fc and Cp); low solubility hampered the measurement of ¹³C NMR. Anal. Calcd for C₆₄H₄₄Fe₄·H₂O: C, 72.90; H, 4.40. Found: C, 72.90; H, 4.49.