# Toward the Development of Molecular Wires: A Terpyridine Spacer Containing Polyferrocenylalkyne Linkages

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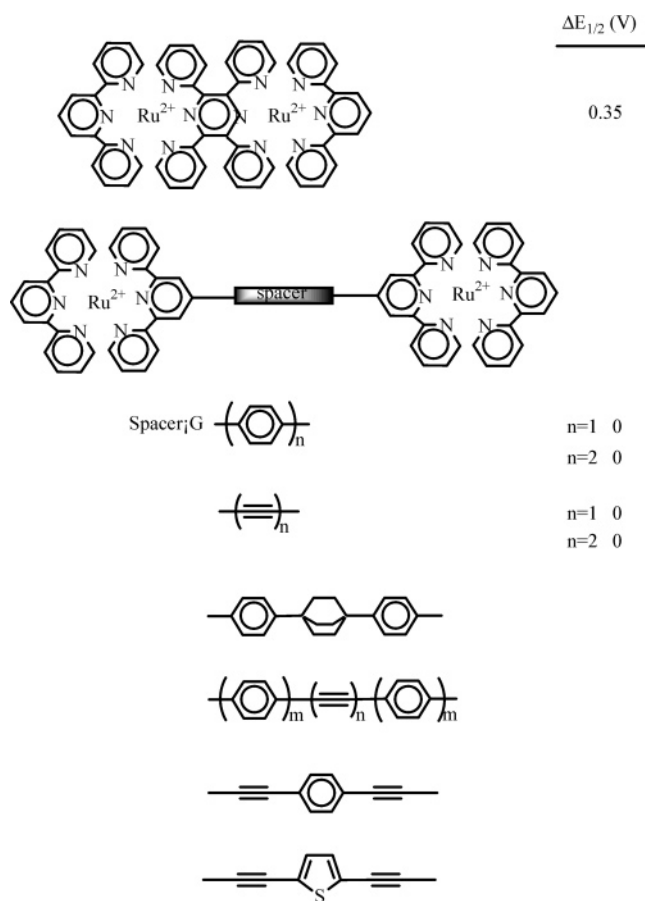Taipei, Taiwan, Republic of China*

The preparation, characterizations, and electrochemical measurements of the terpyridine-ferrocenylalkyne spacers (tpy−C≡C−(fc)$_n$−C≡C−tpy; tpy = terpyridyl; fc = ferrocenyl; $n$ = 2, 3) are described. In the electrochemical measurements, the charge could be delocalized to the cyclopentadienyl and ethynyl moieties caused by the built-up charge density upon oxidation of the ferrocenyl moiety.

## Introduction

Recently, the design of interesting bis(2,2′:6′,2″-terpyridine) (tpy−tpy) ligands by connecting two terpyridine moieties via a spacer attached to their 4′-positions has received a surge in interest,[1−3] owing to their utility in the field of molecular electronics and artificial photosynthesis.[4,5] Our interest in the design of materials for application in molecular wires has focused on how to arrange organometallic redox-active spacers to enhance the capability of transfering information along the molecular axis.[6−10] We are concerned with how best to interlock the ferrocene subunit into an ordered array that permits controlled transfer of stored information. In the past, the wires containing the tpy−tpy ligands have been prepared by combining the most unsaturated form of organic linear spacer with electroactive transition metal terminals (see Chart 1).[11−24] On
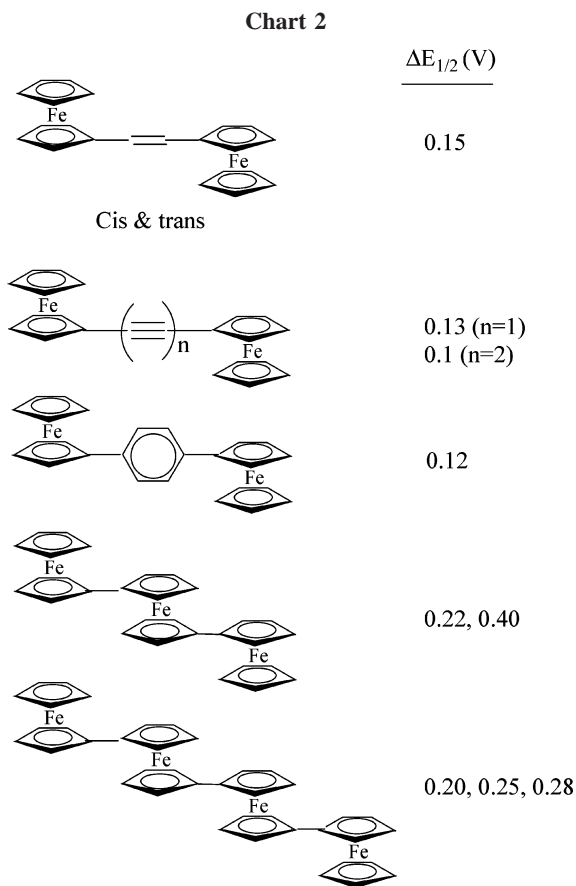
**Chart 1**

the basis of the electrochemical measurements, we believe that ferrocene appears to be a more promising bridge that can ensure fast and quantitative transfer of information within the array

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**Chart 2**

$\Delta E_{1/2}$ (V)



0.15

Cis & trans

0.13 (n=1)
0.1 (n=2)

0.12

0.22, 0.40

0.20, 0.25, 0.28

**Chart 3**



**1a**        **1b**        **1c**

**1b**

□ : ferrocenyl ; ○ : Ru (II) ; ◁ : terpyridinyl ligand

than general unsaturated organic spacers. Electrochemistry has been used as a screening technique (commonly cyclic voltammetry) to investigate metal−metal interactions.[25] As shown in Chart 2, one can apply the redox-active ferrocenyl groups as built-in electrochemical sensors to evaluate the degree of electronic communication through a spacer. It has been demonstrated that the magnitude of the difference ($\Delta E_{1/2}$) of the half-wave potentials ($E_{1/2}$) between two redox waves gives an indication of the interaction between the metal sites: the larger the $\Delta E_{1/2}$ value, the greater the metal−metal interactions (see Charts 1 and 2). The value of $\Delta E_{1/2}$ depends on the separation between the metal centers and the degree of conjugation in the spacer linking the ferrocenes.[26]

Very recently, we have reported[8,10] the preparation of multinuclear supramolecules assembled from 1,1′-bis(terpyridyl)ferrocene(s) redox-active subunits with $Ru^{2+}$ metal centers (Chart 3). As expected, the redox behavior of **1** is dominated by $Ru^{2+}/Ru^{3+}$ redox couples ($E_{1/2}$ from 1.35 to 1.38 V), $Fe^{2+}/Fe^{3+}$ redox couples ($E_{1/2}$ from 0.4 to 1.0 V), and tpy/tpy$^-$/tpy$^{2-}$ redox couples ($E_{1/2}$ from −1.3 to −1.5 V). Attachment of ferrocenyl moieties to the 4′-position of tpy in $Ru^{2+}$ complexes has minimal influence on the $Ru^{2+}/Ru^{3+}$ redox potential (from 1.35 to 1.38 V). These $Ru^{2+}$-centered oxidation processes are more positive by at least 80 mV compared to those of [Ru(tpy)$_2$]$^{2+}$. For the binuclear $Ru^{2+}$ complexes of tpy−(fc)$_n$−tpy, a single wave is found for the $Ru^{2+}/Ru^{3+}$ redox couple, a fact that might indicate that the electronic coupling between the $Ru^{2+}$ centers is relatively weak. Very recently, the physical properties of a series of linearly arranged $Ru^{2+}$ complexes, [(tpy)Ru(tpy−(DEDBT)$_n$−tpy)Ru(tpy)]$^{4+}$ ($n$ = 1, 2, 3, 4, 5), featuring $Ru^{2+}$-tpy chromophores connected to $\pi$-conjugated organic 2,5-diethynyl-3,4-dibutylthiophene oligomeric fragments (DEDBT), have been reported.[21] In these diethynyl-thiophene-bridged complexes, a single wave of the $Ru^{2+}/Ru^{3+}$ redox couple was also found at ∼1.36 V. The electronic coupling between the $Ru^{2+}$ centers in the tpy−DEDBT−tpy system is also relatively weak. However, in our case there were appreciable variations detected in the potentials associated with the $Fe^{2+}/Fe^{3+}$ redox couples in complexes **1a**−**c**. The variations of the $\Delta E_{1/2}$ values and the appreciable variations detected in the $Fe^{2+}/Fe^{3+}$ oxidation potentials strongly suggest that there is an interaction between the spacer and the $Ru^{2+}$ centers. The positive potential shift of the $E_{1/2}$ values for the $Fe^{2+}/Fe^{3+}$ redox couples upon coordination of the $Ru^{2+}$ ion with the free ligand indicates that there is an interaction between $Ru^{2+}$ and $Fe^{2+}$ centers. We suggest that the ferrocenyl spacer plays a more sensitive role to gauge the interaction between the $Ru^{2+}$ and $Fe^{2+}$ centers. This is possible due to the existence of weak back-bonding of the $Fe^{2+}$ metal center to the tpy ligand. Furthermore, the decreasing of the $\Delta E_{1/2}$ values indicates that the magnitude of

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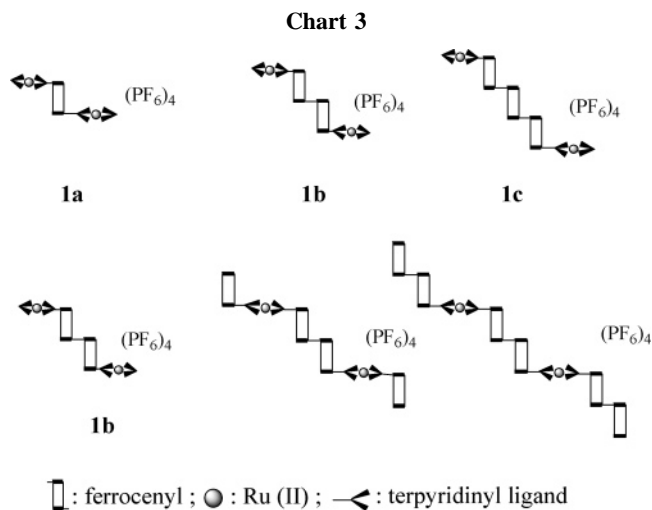
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**Scheme 1**



**Scheme 2**
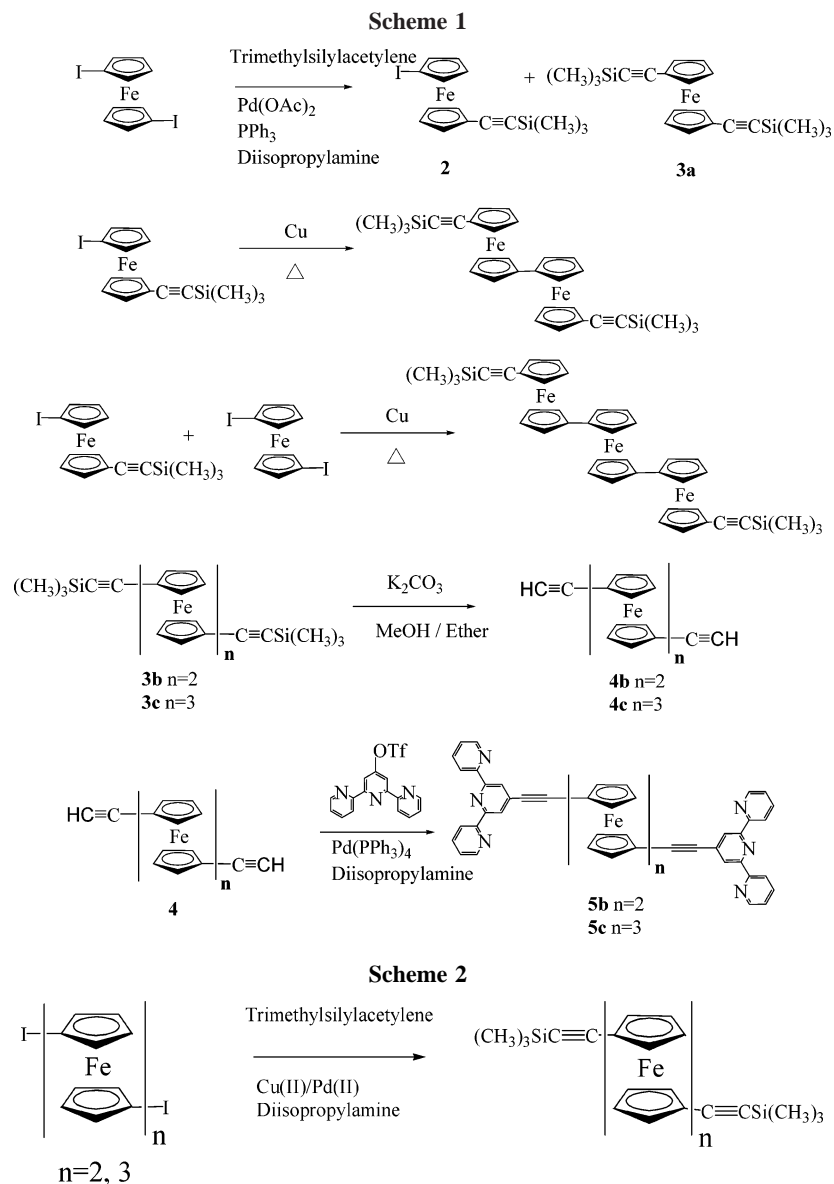


the Fe−Fe interaction is changed pronouncedly upon coordination of the $Ru^{2+}$ ion.

In attempting to perturb the electronic properties of the spacer, we now describe the first step in the preparation of the polyferrocenylalkyne linkages (tpy−C≡C−(fc)$_n$−C≡C−tpy, fc = ferrocene, $n$ = 2, 3). Compounds of tpy−C≡C−(fc)$_n$−C≡C−tpy potentially have the capability to coordinate transition metals, demonstrating versatility in molecule assembly and generation of various composites. Expansion of this study to manipulate the energetics between the terminal metal center, such as $Ru^{2+}$ and $Fe^{2+}$ ions, and the connecting spacer is underway and will be reported in due course.

## Results and Discussion

**Preparations.** As shown in Scheme 1, compounds of the polyferrocenylalkyne linkages (tpy−C≡C−(fc)$_n$−C≡C−tpy, fc = ferrocene, $n$ = 2, 3) were prepared from 1-trimethylsilyl-ethynyl-1′-iodoferrocene (**2**). As shown in Scheme 2, Robinson,[27] Long,[28] and their co-workers have reported the preparation of **3b,c** from corresponding diiodobiferrocene and diiodotriferrocene by using the Cu(II)/Pd(II)-catalyzed coupling of a terminal trimethylsilylacetylene to give desired bis(trimethyl-silylethynyl)ferrocenes. In our experience the yields in the

preparation of iodinated ferrocenyl compounds (diiodobifer-rocene and diiodotriferrocene) were quite variable (0%−5%) and they degraded on silica or alumina during the chromato-graphic separation. Furthermore, diiodotriferrocene was mod-erately unstable. Our strategic regent was 1-trimethylsilylethynyl-1′-iodoferrocene (**2**), which was prepared by using Pd(II)-catalyzed coupling of trimethylsilylacetylene to 1,1′-diiodo-ferrocene. Thus, Ullmann coupling of **2** gave the desired bisethynylferrocenes **3b,c** in good yields. Unsubstituted bis-acetyllide species **4** were prepared in excellent yield (75%) by straightforward addition of $K_2CO_3$ to a solution of **3** in methanol and diethyl ether. The target compounds of 1,1′-bis(terpyridyl-ethynyl)ferrocenes (**5**) were prepared by the Pd(II)-catalyzed coupling of **4** to 4′-[[(trifluoromethyl)sulfonyl]oxy]-2,2′:6′,2″-terpyridine in ∼30% yields.

**Molecular Structure of 5c.** The X-ray structure of **5c** shows that it is $P\bar{1}$ at 298 K. Complete tables of positional parameters, bond distances, and bond angles are given as Supporting

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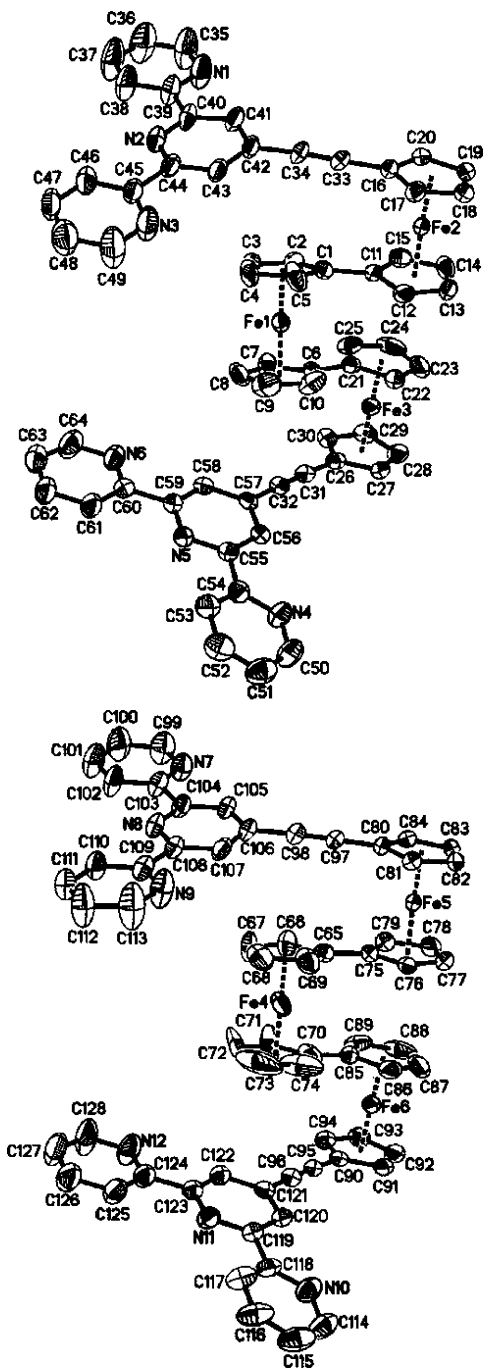
**Figure 1.** Molecular view of **5c**.

Information. As shown in Figure 1, there are two independent molecules in the unit, and the ORTEP view confirms the molecular structure with the triferrocenyl group directly linked to the acetylene linkage, which is linked to the 4′-position of the 2,2′:6′,2″-terpyridine. The triferrocenyl moiety exists in a trans conformation with the two iron ions on opposite sides of the fulvalenide ligand. The two least-squares-fitting Cp planes in a given ferrocenyl moiety are nearly parallel, and the dihedral angles are from 0.66° to 3.68° with an average value of 2.16°. Inspection of the average distances of Fe−C (2.038(8) Å) and Fe−Cp (1.650 Å) indicates that the metallocenes are in the $Fe^{2+}$ oxidation state. The bonds and angles about the Cp rings vary little, and they are close to those reported for analogous ferrocenes.[29] Furthermore, the two Cp rings associated with Fe1
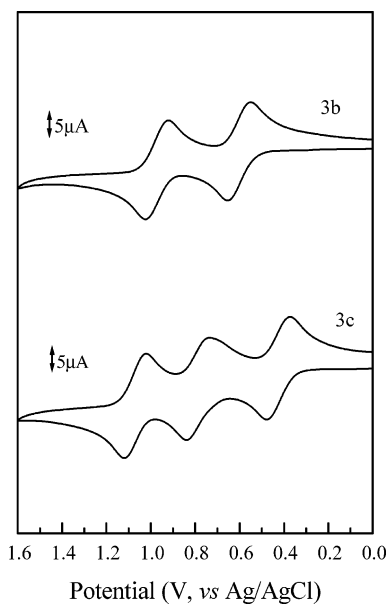


**Figure 2.** Cyclic voltammetric measurements of **3b** and **3c**, recorded with a stationary Pt working electrode. These experiments were carried out with a $1 \times 10^{-3}$ M solution of $CH_2Cl_2$ containing 0.1 M $(n\text{-}C_4H_9)_4NPF_6$ as supporting electrolyte with a scan rate of 0.1 V s$^{-1}$.

and Fe6 are staggered, with average staggering angles of 35.11° and 28.89°, respectively. However, the two Cp rings associated with Fe2, Fe3, Fe4, and Fe5 are nearly eclipsed, with an average staggering angle of 7.11°, 10.64°, 11.62°, and 13.29°.

The 2,2′:6′,2″-terpyridine group adopts the expected trans−trans conformation about the interannular bonds.[30,31] The pyridyl units in each terpyridine group are not completely coplanar, and the dihedral angles are from 0.58° to 15.39° with an average value of 6.93°. The Cp ring of the ethynylferrocene group is also not coplanar with the central pyridyl ring of terpyridine, and the dihedral angles are from 12.46° to 17.49° with an average value of 15.62°.

**Electrochemical Measurements.** As shown in Figures 2−4, the series of ferrocenyl compounds (**3−5**) exhibit quite interesting electrochemical behavior. In the case of trimethylsilylethynyl compounds (**3b** and **3c**), reversible ferrocene-based one-electron oxidations have been observed in $CH_2Cl_2$ solution ($E_{1/2} = 0.60$, 0.97 for **3b**; $E_{1/2} = 0.42$, 0.78, 1.07 V for **3c**, vs Ag/Ag$^+$). Furthermore, ethynylbiferrocenyl compounds (**4b** and **5b**) undergo two separate redox steps, having features of full chemical reversibility ($E_{1/2} = 0.61$, 0.98 for **4b**; $E_{1/2} = 0.61$, 1.00 V for **5b**, vs Ag/Ag$^+$). An interesting finding for ethynyl-triferrocenyl compounds of **4c** and **5c** is that the oxidation of the third ferrocenyl moiety at potential ∼1.1 V has a pronounced influence on the electrochemical behavior. As shown in Figure 4, in $CH_2Cl_2$ solution they undergo two reversible ferrocene-based one-electron oxidations, recorded at potentials from 0.0 to 1.0 V with a scan rate of 0.1 V s$^{-1}$ ($E_{1/2} = 0.42$, 0.84 for **4c**; $E_{1/2} = 0.42$, 0.86 V for **5c**, vs Ag/Ag$^+$). As the scanning potential is increased to 1.8 V, a symmetry sharp peak develops at a potential of ∼0.7 V. Repeat scanning does not change the voltammograms, demonstrating that compounds are stable to electrochemical cycling in $CH_2Cl_2$ solution. This observation has not been found in the cases of **4b**, **5b**, and 1,1′-bis-

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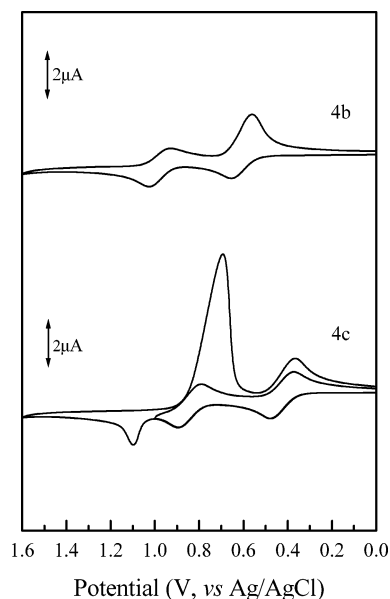
**Figure 3.** Cyclic voltammetric measurements of **4b** and **4c**, recorded with a stationary Pt working electrode. These experiments were carried out with a $1 \times 10^{-3}$ M solution of $CH_2Cl_2$ containing 0.1 M ($n$-$C_4H_9$)$_4$NPF$_6$ as supporting electrolyte with a scan rate of 0.1 V s$^{-1}$.
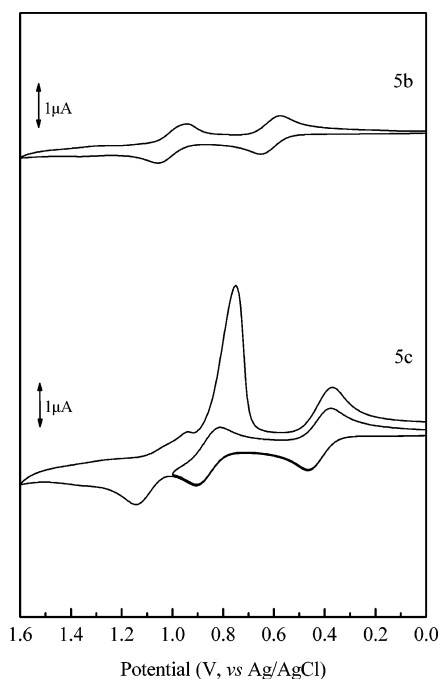


**Figure 4.** Cyclic voltammetric measurements of **5b** and **5c**, recorded with a stationary Pt working electrode. These experiments were carried out with a $1 \times 10^{-3}$ M solution of $CH_2Cl_2$ containing 0.1 M ($n$-$C_4H_9$)$_4$NPF$_6$ as supporting electrolyte with a scan rate of 0.1 V s$^{-1}$. Under these conditions, ferrocene shows a reversible one-electron redox wave ($E_{1/2} = 0.46$ V).

(terpyridyl)triferrocene ($E_{1/2} = 0.37, 0.77, 1.04$ V vs Ag/Ag$^+$).[8,10] As illustrated in Scheme 3, we would like to suggest that the charge could be delocalized to the cyclopentadienyl and ethynyl moieties caused by the built-up charge density upon the third oxidation of the ferrocenyl moiety.

One of the interesting attributes of **5b** and **5c** is the magnitude of the electronic interaction between the Fe sites. Cyclic voltammetry affords a simple and effective way for estimating this interaction. It has been demonstrated that the magnitude of

the peak-to-peak separation ($\Delta E_{1/2}$) gives an indication of the interaction between the metal sites in the solution state.[26] A comparison of the $\Delta E_{1/2}$ of **5b** (0.39 V) and **5c** (0.44 V) with corresponding 1,1′-bis(terpyridyl)biferrocene (0.43 V) and 1,1′-bis(terpyridyl)triferrocene (0.40 and 0.27 V) indicates that the magnitude of interaction between the Fe sites in the *solution state* in **5b** and **5c** is changed by the ethynyl moiety. This indicates that the interaction between the Fe sites is sensitive to the nature of the ethynyl moiety. Thus, the electronic property of the spacer is perturbed.

## Experimental Section

**General Information.** All manipulations involving air-sensitive materials were carried out by using standard Schlenk techniques under an atmosphere of N$_2$. Solvents were dried as follows: THF and ether were distilled from Na/benzophenone; CH$_2$Cl$_2$ was distilled from CaH$_2$; diisopropylamine and TMEDA were distilled from KOH. Samples of 1,1′-diiodoferrocene and 4′-[[(trifluoromethyl)sulfonyl]oxy]-2,2′:6′,2″-terpyridine were prepared according to the literature procedures.[32,33]

**Preparation of 1-Trimethylsilylethynyl-1′-iodoferrocene (2).** To a stirred solution of diiodoferrocene (4.0 g, 9 mmol) in dried diisopropylamine (60 mL) at 4 °C was added trimethylsilylacetylene (0.65 mL, 4.5 mmol) followed by CuI (0.017 g, 1% mol), Pd(OAc)$_2$ (0.02 g, 1% mol), and PPh$_3$ (0.072 g, 3%). The reaction mixture was stirred for a further 30 min at 4 °C and then refluxed for 24 h. After cooling to room temperature, diethyl ether was added, and then the solution was filtered. The solvent was removed under reduced pressure. The crude product was redissolved in diethyl ether and washed sequentially as follows: 0.1 M HCl (2 × 90 mL), H$_2$O (2 × 100 mL), 0.1 M NaHCO$_3$ (2 × 60 mL), and H$_2$O (2 × 100 mL). The organic layer was dried over MgSO$_4$. After evaporation of the solvent, the crude product was chromatographed on silica, eluting with hexane/CH$_2$Cl$_2$ (90/10). The second band was the desired compound **2**. The yield was approximately 46%. The third band eluting with hexane/CH$_2$Cl$_2$ (80/20) gave compound **3a** (14% yield). The physical properties of **2** are as follows. $^1$H NMR (CDCl$_3$): $\delta$ 0.25 (s, 9H, −SiMe$_3$), 4.20 (d, 4H, $J = 6.0$ Hz, Cp), 4.40 (d, 4H, $J = 6.0$ Hz, Cp). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 0.20 (s, CH$_3$), 29.67 (s, Cp), 40.47 (s, Cp), 67.01 (s, −C≡C−Si−), 71.22 (s, Cp), 72.00 (s, Cp), 74.40 (s, Cp), 91.78 (s, Cp), 102.75 (s, −C≡C−Si−). MS (FAB): M$^+$ at $m/z$ 408. The physical properties of **3a** are as follows. $^1$H NMR (CDCl$_3$): $\delta$ 0.24 (s, 18H, −SiMe$_3$), 4.20 (d, 4H, $J = 2.0$ Hz, Cp), 4.39 (d, 4H, $J = 2.0$ Hz, Cp). MS (FAB): M$^+$ at $m/z$ 378.

**Preparation of 1,1′-Bis(trimethylsilylethynyl)biferrocene, 3b.** A mixture of **2** (0.8 g, 1.96 mmol) and activated copper (5 g) was heated under N$_2$ at 130−140 °C for 24 h. After cooling to room temperature, the reaction mixture was repeatedly extracted with CH$_2$Cl$_2$ until the extracts appeared colorless. The combined extracts were evaporated and chromatographed on neutral alumina (act. III). The first band eluting with hexane was the ferrocenes. The second band eluting with CH$_2$Cl$_2$/hexane (2:8) was the desired compound **3b**. The yield was approximately 40%. The physical properties of **3b** are as follows. $^1$H NMR (CDCl$_3$): $\delta$ 0.24 (s, 18H, −SiMe$_3$), 4.02 (t, 4H, $J = 1.8$ Hz, Cp), 4.20 (t, 4H, $J = 1.8$ Hz, Cp), 4.23 (t, 4H, $J = 2.0$ Hz, Cp), 4.38 (t, 4H, $J = 2.0$ Hz, Cp). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 0.26 (s, CH$_3$), 65.23 (s, −C≡C−Si−), 68.79 (s, α-Cp), 70.03 (s, β-Cp), 70.06 (s, β′-Cp), 73.06 (s, α′-Cp), 84.34 (s, ipso-Cp), 90.55 (s, ipso′-Cp), 104.15 (s, −C≡C−Si−). MS (FAB): M$^+$ at $m/z$ 562. Anal. Calcd for C$_{30}$H$_{34}$Fe$_2$Si$_2$: C, 64.06; H, 6.09. Found: C, 64.25; H, 6.25. Mp: 133.0−135.0 °C.

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**Scheme 3**

X-C≡C-fc-fc-fc-C≡C-X

$E_{1/2}=0.42V$

X-C≡C-fc⁺-fc-fc-C≡C-X  ⇌  X-C≡C-fc-fc⁺-fc-C≡C-X  ⇌  X-C≡C-fc-fc-fc⁺-C≡C-X

$E_{1/2}=0.85V$

X-C≡C-fc⁺-fc⁺-fc-C≡C-X  ⇌  X-C≡C-fc⁺-fc-fc⁺-C≡C-X  ⇌  X-C≡C-fc-fc⁺-fc⁺-C≡C-X

$E_{ox}=1.1V$

fc = ferrocenyl; X = -H; -terpyridyl

**Preparation of 1,1′-Bis(trimethylsilylethynyl)triferrocene, 3c.** A mixture of **2** (1.00 g, 2.45 mmol), 1,1′-diiodoferrocene (0.55 g, 1.25 mmol), and activated copper (15 g) was heated under $N_2$ at 130−140 °C for 24 h. After cooling to room temperature, the reaction mixture was repeatedly extracted with $CH_2Cl_2$ until the extracts appeared colorless. The combined extracts were evaporated and chromatographed on neutral alumina (act. III). The first band eluting with hexane was the ferrocenes. The second band eluting with $CH_2Cl_2$/hexane (25:75) was compound **3b** (34% yield). Continued elution gave the desired compound **3c**. The yield was approximately 12%. The physical properties of **3c** are as follows. ¹H NMR (CDCl₃): δ 0.20 (s, 18H, −SiMe₃), 3.95 (s, 5H, Cp), 4.13 (s, 16H, Cp), 4.27 (s, 3H, Cp). MS (FAB): M⁺ at m/z 746. Anal. Calcd for C₄₀H₄₂Fe₃Si₂: C, 64.36; H, 5.67. Found: C, 64.66; H, 5.25. Mp: 176−178 °C.

**Preparation of 1,1′-Bis(ethynyl)biferrocene (4b).** Compound **2** (0.3 g, 0.53 mmol) was dissolved in a mixture of methanol/diethyl ether (60:40 mL). To this solution was added K₂CO₃ (0.12 g, 0.87 mmol), and the mixture was stirred for 24 h at room temperature. The solvents were removed in vacuo, and the mixture was redissolved in diethyl ether and washed with H₂O (2 × 50 mL). The organic layer was dried over MgSO₄. After evaporation of the solvent, the crude product was chromatographed on silica, eluting with hexane/CH₂Cl₂ (1:1). The first band wires compound **4b**. The yield was approximately 77%. The physical properties of **4b** are as follows. ¹H NMR (CDCl₃): δ 2.67 (s, 2H, −C≡CH), 4.03 (t, 4H, J = 2.0 Hz, Cp), 4.23 (t, 4H, J = 1.8 Hz, Cp), 4.26 (t, 4H, J = 1.8 Hz, Cp), 4.41 (s, 4H, J = 2.0 Hz, Cp). ¹³C{¹H} NMR (CDCl₃): δ 64.37 (s, −C≡C−H), 68.39 (s, α-Cp), 69.96 (s, β-Cp), 70.04 (s, β′-Cp), 72.98 (s, α′-Cp), 73.78 (s, ipso′-Cp), 82.39 (s, −C≡C−H), 84.26 (s, ipso-Cp). MS (FAB): M⁺ at m/z 418. Anal. Calcd for C₂₄H₁₈Fe₂: C, 68.95; H, 4.34. Found: C, 69.15; H, 4.08. Mp: 114.0−116.0 °C.

**Preparation of 1,1′-Bis(ethynyl)triferrocene (4c).** Preparation of **4c** was carried out in a manner similar to that for compound **4b**. The crude product was purified by chromatography on Al₂O₃ (act. III), eluting with hexane/CH₂Cl₂ (3:2). The yield was approximately 75%. The physical properties of **4c** are as follows. ¹H NMR (CDCl₃): δ 2.66 (s, 2H, −C≡CH), 3.98 (s, 4H, Cp), 4.17 and 4.21 (s, 16H, Cp), 4.34 (s, 4H, Cp). ¹³C{¹H} NMR (CDCl₃): δ 64.36 (s, −C≡C−H), 67.57 (s, Cp), 68.14 (s, Cp), 69.85 (s, Cp), 70.06 (s, Cp), 72.90 (s, Cp), 73.70 (s, Cp), 82.50 (s, −C≡C−H), 85.23 (s, Cp). MS (FAB): M⁺ at m/z 602. Anal. Calcd for C₃₄H₂₆Fe₃: C, 67.82; H, 4.35. Found: C, 67.78; H, 3.94. Mp: 150−152 °C.

**Preparation of 1,1′-Bis(terpyridylethynyl)biferrocene (5b).** To a stirred solution of **4b** (0.1 g, 0.24 mmol) and 4′-[[(trifluoromethyl)-sulfonyl]oxy]-2,2′:6′,2′′-terpyridine (0.18 g, 0.48 mmol) in dried THF (20 mL) were added dried diisopropylamine (3.5 mL) and Pd(PPh₃)₄ (0.016 g, 0.0144 mmol). The reaction mixture was refluxed for 16 h. After cooling to room temperature, the solution was filtered. The solvent was removed under reduced pressure. The crude product was extracted with CH₂Cl₂. The organic layer was dried over MgSO₄. After evaporation of the solvent, the crude product was chromatographed on neutral alumina (act. III), eluting

with CH$_2$Cl$_2$/MeOH (95/5). The third band was the desired compound **5b**. The yield was approximately 30%. The physical properties of **5b** are as follows. $^1$H NMR (CDCl$_3$): δ 4.11 (t, 4H, *J* = 2 Hz, β'-Cp), 4.24 (t, 4H, *J* = 2 Hz, β-Cp), 4.32 (t, 4H, *J* = 2 Hz, α'-Cp), 4.47 (t, 4H, *J* = 2 Hz, α-Cp), 7.3 (ddd, 4H, *J* = 7.5, 4.9, 1.5 Hz, tpy-H$_{5,5''}$), 7.86 (td, 4H, *J* = 7.8, 2.00 Hz, tpy-H$_{4,4''}$), 8.44 (s, 4H, tpy-H$_{3',5'}$), 8.61 (d, 4H, *J* = 8.0 Hz, tpy-H$_{3,3''}$), 8.72 (d, 4H, *J* = 4.0 Hz, tpy-H$_{6,6''}$). $^{13}$C{$^1$H} NMR (CDCl$_3$): δ 64.79 (s, ipso'-Cp), 68.16 (s, α-Cp), 70.04 (s, β-Cp), 70.57 (s, β'-Cp), 72.90 (s, α'-Cp), 84.28 (s, −C≡C−tpy), 84.60 (s, ipso-Cp), 93.88 (s, −C≡C−tpy), 121.16 (s, tpy-C$_{3,3''}$), 122.55 (s, tpy-C$_{3',5'}$), 123.87 (s, tpy-C$_{5,5''}$), 134.25 (s, tpy-C$_{4'}$), 136.83 (s, tpy-C$_{4,4''}$), 149.17 (s, tpy-C$_{6,6''}$), 155.27 (s, tpy-C$_{2',6'}$), 155.89 (s, typ-C$_{2,2''}$). MS (FAB): M$^+$ at *m/z* 880. Anal. Calcd for C$_{54}$H$_{36}$N$_6$Fe$_2$: C, 73.65; H, 4.12; N, 9.54. Found: C, 73.24; H, 4.12; N, 9.32. Mp: 230 (dec) °C.

**Preparation of 1,1'-Bis(terpyridylethynyl)triferrocene (5c).** Preparation of **5c** was carried out in a manner similar to that for compound **5b**. The crude product was chromatographed on neutral alumina (act. IV), eluting with CH$_2$Cl$_2$/hexane (80/20). The third band was the desired compound **5c**. The yield was approximately 25%. The physical properties of **5c** are as follows. $^1$H NMR (CDCl$_3$): δ 3.98 (t, 4H, *J* = 1.5 Hz, Cp), 4.04 (t, 4H, *J* = 1.5 Hz, Cp), 4.11 (t, 4H, *J* = 1.5 Hz, Cp), 4.17 (t, 4H, *J* = 1.5 Hz, Cp), 4.23 (t, 4H, *J* = 1.5 Hz, Cp), 4.26 (t, *J* = 1.5 Hz, Cp), 7.35 (ddd, 4H, *J* = 6.8, 4.5, 1.0 Hz, tpy-H$_{5,5''}$), 7.87 (td, 4H, *J* = 7.8, 1.7 Hz, tpy-H$_{4,4''}$), 8.43 (s, 4H, tpy-H$_{3',5'}$), 8.62 (d, 4H, *J* = 8.0 Hz, tpy-H$_{3,3''}$), 8.73 (d, 4H, *J* = 4.0 Hz, tpy-H$_{6,6''}$). $^{13}$C{$^1$H} NMR (CDCl$_3$): δ 64.43 (s, Cp), 67.70 (s, Cp), 67.93 (s, Cp), 68.97 (s, Cp), 69.74 (s, Cp), 70.56 (s, Cp), 72.79 (s, Cp), 82.72 (s, Cp), 84.41 (s, −C≡C−tpy), 85.36 (s, Cp), 94.07 (s, −C≡C−tpy), 121.17 (s, tpy-C$_{3,3''}$), 122.53 (s, tpy-C$_{3',5'}$), 123.87 (s, tpy-C$_{5,5''}$), 134.28 (s, tpy-C$_{4'}$), 136.85 (s, tpy-C$_{4,4''}$), 149.16 (s, tpy-C$_{6,6''}$), 155.26 (s, tpy-C$_{2',6'}$), 155.90 (s, typ-C$_{2,2''}$). MS (FAB): M$^+$ at *m/z* 1064. Anal. Calcd for C$_{64}$H$_{44}$N$_6$Fe$_3$: C, 72.20; H, 4.17; N, 7.89. Found: C, 71.92; H, 4.31; N, 7.94. Mp: 236 (dec) °C.

**Physical Methods.** $^1$H NMR spectra were run on a Varian INOVA-500 MHz spectrometer. Mass spectra were obtained with a VG-BLOTECH-QUATTRO 5022 system, and ESI-LCQ mass spectra were obtained with a Thermo Finnigan spectrometer. Electrochemical measurements were carried out with a CHI 660B system. Cyclic voltammetry was performed with a stationary Pt working electrode. These experiments were carried out with a 1 × 10$^{-3}$ M solution of CH$_2$Cl$_2$ containing 0.1 M (*n*-C$_4$H$_9$)$_4$NPF$_6$ as supporting electrolyte. The potentials quoted in this work are relative to the Ag/AgCl electrode at 25 °C. Under these conditions, ferrocene shows a reversible one-electron redox wave ($E_{1/2}$ = 0.46 V).

**Note Added after ASAP Publication.** In the version of this paper posted on the Web March 18, 2006, the word "ethynyl" was misspelled throughout the text. These misspellings have now been corrected.

**Supporting Information Available:** General experimental details, experimental details for the formation of compounds **2**−**5**, and spectroscopic data for compounds **2**−**5**. Complete tables of crystal data collections and unit-cell parameters, positional parameters, and bond distances and angles for **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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