Biferrocenes with Heteroaromatic Spacers: Synthesis, Structure, and Electrochemistry

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Diferrocenyl complexes containing thiophene or furan in the conjugation chain have been synthesized by Wittig, McMurray, and Sonogashira coupling reactions. Ferrocene and the heteroaromatic rings are connected by vinyl or ethynyl linkages. These biferrocenes were characterized by elemental analysis, NMR, optical and mass spectroscopy, and cyclic voltammetric studies. The structure of (η^5-C_5H_5)Fe(η^5-C_5H_4)CH=CHC_4H_2SCH=CH(η^5-C_5H_4)-Fe(η^5-C_5H_5) has been determined by single-crystal X-ray diffraction methods. The interaction between the ferrocene units are weak, and thus in cyclic voltammetry a single two-electron redox process with a larger peak-to-peak separation was observed.

Introduction

There is a growing interest in the study of electron or energy transfer between two redox acive and/or photoactive termini across an unsaturated organic bridge.[1−3] Molecular wires comprising mixed-valence bimetallic fragments could be used for applications in molecular electronics, optoelectronic devices, and chemical sensor appliances.[1] Systems incorporating ruthenium polypyridyl[4] or ferrocene[5] moieties are known with oligoene or oligoyne spacers. Alternations of the bridges with arenes have been explored. In most of the biferrocenes studied, the ferrocene units are linked either directly or using a polyene bridge. If the bridging ligands are phenylene vinylene oligomers, the biferrocenes exhibit rather diminished solubility, and use of permethylated cyclopentadienyl units is necessary to overcome this drawback.[5e] This modification in the cyclopentadienyl moiety could enhance the stability of the oxidized ferrocenium species.

Although, polyalkene species present high electron transmission efficiency, their thermal and photochemical instability poses severe drawbacks. On the other hand, the efficiency of the more stable aromatic and acetylene-based systems appears limited by excessive charge confinement. Thiophene-2,5-diylvinylene oligomers are considered a good tradeoff between the efficiency of polyethylenic systems and the stability of the polyaromatic ones.[6] Due to this, thiophene-based oligomers and polymers are regarded to have potential for technological applications in electrical and optical devices.[7] The solubility of the thiophene derivatives could be increased when warranted by incorporating alkyl chains in the 3- and 4-positions of the thiophene nucleus. Despite these advantages, ferrocene complexes containing thiophene are very limited. We have recently reported a series of donor−acceptor complexes derived from ferrocene and thiophene or furan.[8] In continuation of our attempts toward the design of ferrocene-based materials with thiophene or furan conjugation, we describe here a series of biferrocenes linked by thienyl or furanyl vinyl and thienyl ethynyl spacers.

Experimental Section

General Procedures. All reactions and manipulations were carried out under N_2 with the use of standard inert atmosphere and Schlenk techniques. Solvents were dried by routine procedures. Column chromatography was performed with the use of silica gel (230−400 mesh ASTM, Merck) as the stationary phase in a column of 25 cm length and 4.0 cm diameter. The starting materials used in this study, (ferrocenylmethyl)triphenylphosphonium bromide,[9] 5-(2-ferrocenylvinyl)thiophene-2-carbaldehyde,[8] 5-(2-ferrocenylvinyl)furan-2-carbaldehyde,[8] 2-ferrocenylthiophene,[10] 5-ferrocenylthiophene-2-carbaldehyde,[8] 5,5′-dibromo[2,2′]bithiophene,[11] and 5,5″-dibromo[2,2′;5′,2″]terthiophene,[12] were prepared by adopting

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reported procedures. The NMR spectra were recorded on a Bruker AC300 spectrometer. Optical electronic spectra were measured in dichloromethane using a Cary 50 Probe UV−visible spectrophotometer. Cyclic voltammetry experiments were performed with a BAS-100 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a nonaqueous Ag/$AgNO_3$ reference electrode. The solvent in all experiments was CH_2Cl_2, and the supporting electrolyte was 0.1 M tetrabutylammonium perchlorate. The $E_{1/2}$ values were determined as $1/2(Ep_a + Ep_c)$, where Ep_a and Ep_c are the anodic and cathodic peak potentials, respectively. All potentials reported are with reference to Fc^+/Fc external standard (+0.250 V relative to $Ag/AgNO_3$) and are not corrected for the junction potential. Mass spectra were obtained from a VG70-250S mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

2,5-Bis(2-ferrocenylvinyl)thiophene (1a). A suspension of ferrocenylmethylphosphonium bromide (0.540 g, 1 mmol) in THF (50 mL) maintained at 0 °C was treated with potassium *tert*-butoxide (0.112 g, 1 mmol) with vigorous stirring. The wine red solution was added at once 5-(2-ferrocenylvinyl)thiophene-2-carboxaldehyde (0.320 g, 1 mmol) through a sidearm. The mixture was slowly warmed to room temperature and subsequently refluxed for ca. 8 h. It was then cooled, poured into ice water, and extracted with diethyl ether (3 × 25 mL). The organic extract was washed with aqueous NaCl, dried over anhydrous $MgSO_4$, and evaporated to dryness to yield a brown solid. This was purified using column chromatography (SiO_2, CH_2Cl_2/hexane (1:1)) to yield 0.401 g (80%) of analytically pure sample. Anal. Calcd for $C_{28}H_{24}Fe_2S$: C, 66.69; H, 4.80. Found: C, 66.22; H, 5.07. ^{1}H NMR ($CDCl_3$): 4.13 (s, 10H, Cp), 4.27 (t, 1.7 Hz, 4H, Cp′), 4.41 (t, 1.7 Hz, 4H, Cp′), 6.63 (d, 15.9 Hz, 2H, vinyl), 6.75 (d, 15.6 Hz, 2H, vinyl), 6.76 (s, 2H, thiophene). MS (FAB +ve): *m*/*z* 504 (calcd M^+ 504).

2,5-Bis(2-ferrocenylvinyl)furan (1b). It was obtained in 66% yield as described above but using 5-(2-ferrocenylvinyl)-furan-2-carbaldehyde and ferrocenylmethylphosphonium bromide. Anal. Calcd for $C_{28}H_{24}Fe_2O$: C, 68.89; H, 4.96. Found: C, 68.72; H, 5.01. ^{1}H NMR ($CDCl_3$): 4.14 (s, 10H, Cp), 4.27 (t, 1.7 Hz, 4H, Cp′), 4.43 (t, 1.7 Hz, 4H, Cp′), 6.20 (s, 2H, furan), 6.46 (d, 15.7 Hz, 2H, vinyl), 6.82 (d, 15.9 Hz, 2H, vinyl). MS (FAB +ve): *m*/*z* 488 (calcd M^+ 488).

1,2-Bis(5-ferrocenylvinyl-2-thiophene)ethylene (2a). To a stirred THF solution of 5-(2-ferrocenylvinyl)thiophene-2-carboxaldehyde (0.320 g, 1 mmol) was added $TiCl_4$ (0.19 g, 1 mmol) at 0 °C. After 30 min, zinc powder (0.065 g, 1 mmol) was added through the sidearms, and the mixture was allowed to warm to room temperature over 1 h. It was refluxed for 3 h, cooled, poured into ice water, and extracted with dichloromethane. The combined dichloromethane extracts were washed with brine solution, dried over anhydrous $MgSO_4$, and evaporated to dryness to leave a red residue. It was purified by column chromatography (SiO_2, hexane/dichloromethane, 1:1 mixture) to give 0.280 g (92%). Anal. Calcd for $C_{34}H_{28}Fe_2S_2$: C, 66.68; H, 4.61. Found: C, 67.01; H, 4.72. ^{1}H NMR ($CDCl_3$): 4.13 (s, 10H, Cp), 4.28 (t, 1.7 Hz, 4H, Cp′), 4.42 (t, 1.7 Hz, 4H, Cp′), 6.64 (d, 15.8 Hz, 2H, vinyl), 6.75 (d, 16.0 Hz, 2H, vinyl), 6.79 (d, 3.7 Hz, 2H, thiophene), 6.86 (d, 3.6 Hz, 2H, thiophene), 6.91 (s, 2H, vinyl). MS (FAB +ve): *m*/*z* 613 (calcd M^+ 613).

1,2-Bis(5-ferrocenylvinyl-2-furan)ethylene (2b). It was prepared in 86% yield as described above for **2a** using 5-(2-ferrocenylvinyl)furan-2-carboxaldehyde. Anal. Calcd for $C_{34}H_{28}Fe_2O_2$: C, 70.37; H, 4.86. Found: C, 70.23; H, 4.78. ^{1}H NMR ($CDCl_3$): 4.14 (s, 10H, Cp), 4.30 (t, 1.7 Hz, 4H, Cp′), 4.45 (t, 1.7 Hz, 4H, Cp′), 6.21 (d, 3.2 Hz, 2H, furan), 6.33 (d, 3.2 Hz, 2H, furan), 6.44 (d, 16.0 Hz, 2H, vinyl), 6.82 (d, 16.0 Hz, 2H, vinyl), 6.83 (s, 2H, vinyl). MS (FAB +ve): *m*/*z* 580 (calcd M^+ 580).

2-Ferrocenyl-5-(2-ferrocenylvinyl)thiophene (3). It was prepared from 2-ferrocenylthiophene-5-carbaldehyde and ferrocenylmethylphosphonium bromide in 72% yield as described for **1**. Anal. Calcd for $C_{26}H_{22}Fe_2S$: C, 65.30; H, 4.64. Found: C, 65.21; H, 4.78. ^{1}H NMR (CD_3COCD_3): 4.10 (s, 5H, Cp), 4.14 (s, 5H, Cp), 4.29 (t, 1.7 Hz, 2H, Cp′), 4.32 (t, 1.7 Hz, 2H, Cp′), 4.52 (t, 1.7 Hz, 2H, Cp′), 4.63 (t, 1.7 Hz, 2H, Cp′), 6.66 (d, 15.8 Hz, 1H, vinyl), 6.82 (d, 3.6 Hz, thiophene), 6.89 (d, 15.9 Hz, 1H, vinyl), 6.97 (d, 3.6 Hz, thiophene). MS (FAB +ve): *m*/*z* 478 (calcd M^+ 478).

2,5-Bis(ferrocenylethynyl)thiophene (4a). Ethynylferrocene (0.525 g, 2.5 mmol), 2,5-dibromothiophene (0.302 g, 1.25 mmol), bis(triphenylphosphino)dichloropalladium(II) (0.035 g), cuprous iodide (0.005 g), and diethylamine (50 mL) were charged in a two-necked round-bottomed flask under N_2 atmosphere and refluxed for 12 h. The mixture was cooled and then evaporated to dryness under vacuum. The resulting residue was suspended in water and extracted with dichloromethane. The organic extracts were thoroughly washed with brine solution and dried over anhydrous $MgSO_4$, and the solvent was expelled to give an orange product. It was further purified by column chromatography (SiO2, hexane/dichloromethane (1:1 mixture)). Yield: 0.480 (77%). Anal. Calcd for $C_{28}H_{20}Fe_2S$: C, 67.23; H, 4.03. Found: 67.18; H, 3.87. ^{1}H NMR ($CDCl_3$): 4.24 (brs, 14H, Cp & Cp′), 4.50 (t, 1.7 Hz, 4H, Cp′), 7.02 (s, 2H, thiophene). MS (FAB +ve): *m*/*z* 500 (calcd M^+ 500).

5,5′-Bis(ferrocenylethynyl)[2,2′]bithiophene (4b). It was prepared in 48% yield, as described above, from 5,5′-dibromo-[2,2′]bithiophene. Anal. Calcd for $C_{32}H_{22}Fe_2S_2$: C, 66.00; H, 3.81. Found: 66.15; H, 3.99. ^{1}H NMR (CD_2Cl_2): 4.26 (s, 10H, Cp), 4.29 (t, 1.7 Hz, 4H, Cp′), 4.51 (t, 1.7 Hz, 4H, Cp′), 7.07 (d, 3.7 Hz, 2H, thiophene), 7.12 (d, 3.6 Hz, 2H, thiophene). MS (FAB +ve): *m*/*z* 582 (calcd M^+ 582).

5,5″-Bis(ferrocenylethynyl)[2,2′;5′,2″]terthiophene (4c). A similar procedure as illustrated for **4a** was used to obtain the title compound in 66% yield, from 5,5″-dibromo[2,2′;5′,2″]-terthiophene. Anal. Calcd for $C_{36}H_{24}Fe_2S_3$: C, 65.07; H, 3.64. Found: 64.82; H, 3.78. ^{1}H NMR (CD_2Cl_2): 4.26 (s, 10H, Cp), 4.29 (t, 1.7 Hz, 4H, Cp′), 4.52 (t, 1.7 Hz, 4H, Cp′), 7.08 (d, 3.7 Hz, 2H, thiophene), 7.126 (d, 3.6 Hz, 2H, thiophene), 7.128 (s, 2H, thiophene). MS (FAB +ve): *m*/*z* 664 (calcd M^+ 664).

Structure Determination of 1a·CH_2Cl_2. An orange prismatic crystal of (η^5-C_5H_5)Fe(η^5-C_5H_4)CH=CHC_4H_2SCHCH(η^5-C_5H_4)Fe(η^5-C_5H_5)·CH_2Cl_2 (**1a**) (dimensions 0.28 × 0.22 × 0.13 mm^3) was grown from a room-temperature dichloromethane solution layered with hexane. Crystal, data collection, and refinement parameters are summarized in Table 1. The orthorhombic space group *Pnma* was determined from systematic absences; successful refinement of the structure confirmed the space group assignment. Heavy atom methods were used to locate the Fe and sulfur atoms, while subsequent cycles of least-squares refinements and difference Fourier map were used to locate the remaining non-hydrogen atoms. Hydrogen atoms were placed at calculated positions. All calculations were performed using the NRCVAX[13] software package. Relevant experimental details are listed in Table 1. All other crystal data for **1a**·CH_2Cl_2 are given in the Supporting Information.

Results and Discussion

Synthesis, Spectra, and Structure. The complexes **1a**, **1b**, and **3** were synthesized by the Wittig reaction of ferrocenylmethylphosphonium bromide with the corresponding aldehydes (**A**, **B**, and **C**) (Scheme 1). Simi-

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Scheme 1

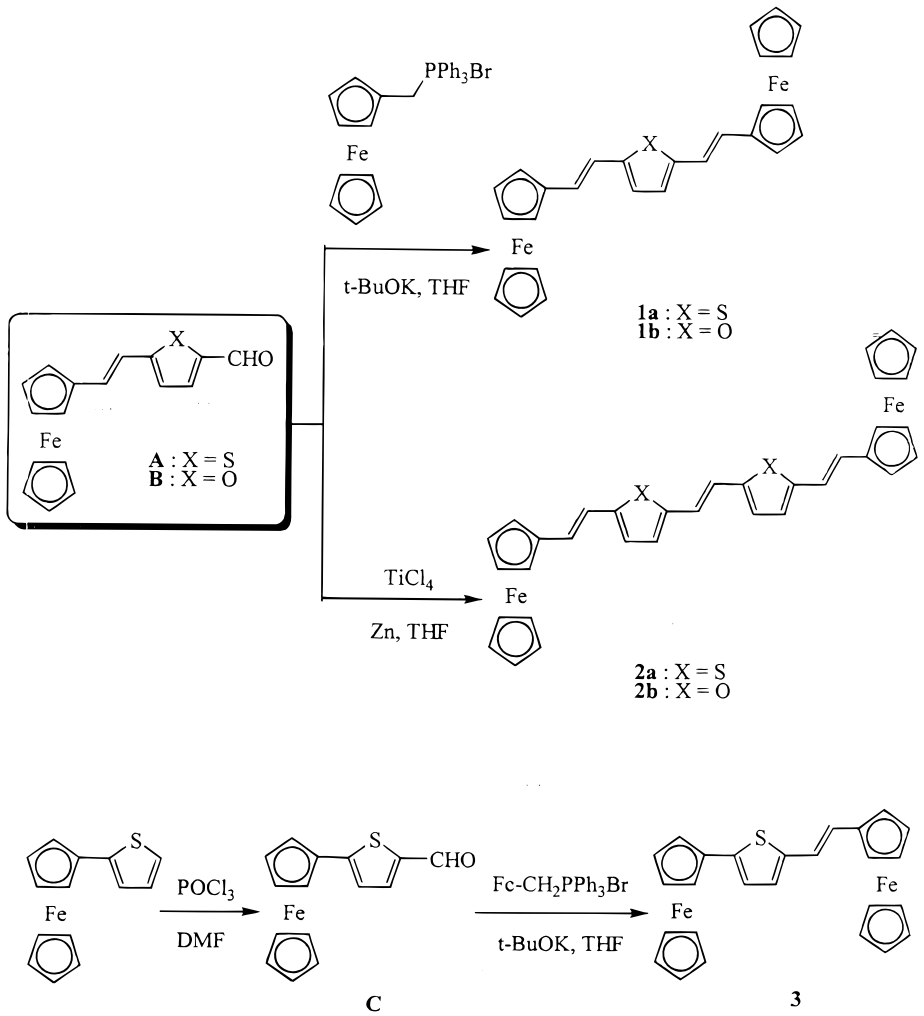

Table 1. Crystal and Refinement Data for 1a

chemical formula	$C_{29}H_{26}Cl_2Fe_2S$
fw	589.18
lattice type	orthorhombic
space group	*Pnma*
a, Å	13.5058(22)
b, Å	32.130(7)
c, Å	5.8255(23)
V, Å^3	2527.9(12)
ρ_{calc}, g/cm^3	1.548
μ, cm^{-1}	14.57
$\lambda_{Mo\ K\alpha}$, Å	0.70930
T, °C	25
GOF	2.43
R^a	0.065
$R_w{}^b$	0.076

^{a} $R = \{\sum(||F_o| - |F_c||)\}/\{\sum|F_o|\}$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2]^{1/2}/\{\sum wF_o{}^2\}$, where $w = (1/\sigma^2)(F_o)$ and the quantity minimized was $\sum w(|F_o| - |F_c|)^2$.

larly, McMurray reactions of **A** and **B** using $TiCl_4$ and Zn provided the diferrocenes **2a** and **2b** in excellent yields. Use of McMurray reactions for the construction of the organometallic conjugated segment is rather rare.[5e] The success of the preparation of **2a** and **2b** points out that this method is very useful for the doubling of conjugation length in the organometallic molecular wires, in particular those with ferrocene end groups. The compounds 2,5-bis(ferrocenylethynyl)thiophene (**4a**), 5,5′-bis(ferrocenylethynyl)[2,2′]-bithiophene (**4b**), and 5,5″-bis(ferrocenylethynyl)[2,2′;5′,2″]terthiophene (**4c**) were formed by the Sonogashira coupling reactions of ethynylferrocene with the corresponding dibromothiophenes (Scheme 2). Strict anaerobic conditions are necessary to prevent the formation of 1,4-diferrocenylbutadiyne, a homocoupling product.[5g] After purification by column chromatography, the compounds were isolated as orange or red air- and moisture-stable microcrystalline solids. The solubility of **1**−**4** in chlorocarbon solvents decreases with increasing number of thiophene units and vinyl fragments. Thus, the compounds **2a** and **2b** exhibited diminished solubility in dichloromethane when compared to **4c**.

The NMR spectral features are in accordance with the symmetrical nature of the compounds and show the presence of ferrocene, thiophene, and vinyl moieties. The electronic spectra of the complexes were measured for dichloromethane solutions, and the data are presented in Table 2. In general the complexes display two absorption bands. The lower energy weak absorption is attributed to the d−d transition,[14] while the higher energy intense band arises from $\pi-\pi^*$ transition of the heteroaromatic segments.[6c] This assignment is further supported by the fact that extension of conjugation leads to bathochromic shift of the $\pi-\pi^*$ transition and a sharp increase in the molecular extinction coefficient (Figure

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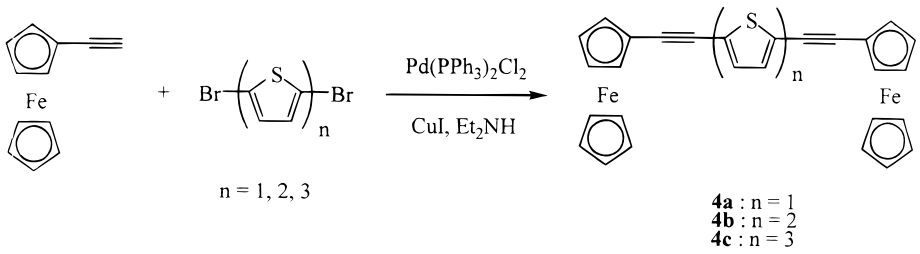
Scheme 2



n = 1, 2, 3

4a : n = 1
4b : n = 2
4c : n = 3

Table 2. Electronic Spectral and Electrochemical Data for the Biferrocenes

compound	λ_{max} ($\epsilon \times 10^{-3}$)[a]	E_{ox} (ΔEp)[b]
1a	471 (6.74)	−0.020 (197)
	396 (26.34)	0.819
1b	462 (6.98)	−0.030 (169)
	391 (36.37)	0.732
2a	502 (sh)	−0.026 (162)
	436 (22.94)	0.560
	336 (14.90)	0.777
2b	491 (sh)	−0.035 (156)
	431 (26.39)	0.342 (92)
	329 (17.37)	
3	462 (4.42)	−0.033 (113)
	371 (24.86)	0.089 (102)
		0.910
4a	445 (3.40)	0.141 (170)
	340 (26.69)	1.026
4b	450 (sh)	0.131 (163)
	385 (32.41)	0.917
4c	412 (44.72)	0.125 (149)
		0.690

[a] λ_{max} in nm and ϵ in M^{-1} cm^{-1} for dichloromethane solutions (5×10^{-5} M). [b] All the potential values are with reference to Fc^+/Fc external standard. $E_{ox} = (Ep_c + Ep_a)/2.0$ for reversible oxidation, and peak potential is reported for irreversible oxidation (in volts). ΔEp in mV. All the data are taken from a 100 mV/s scan for 0.001 M sample solutions in dichloromethane with 0.1 M tetrabutylammonium perchlorate as electrolyte.

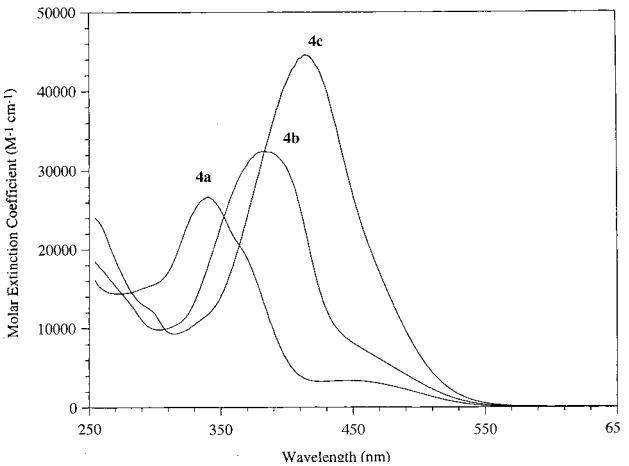


Figure 1. Absorption spectra of the compounds **4a**, **4b**, and **4c**.

1). Thus, for **4c**, λ_{max} and ϵ reach values of 412 nm and 44 720 M^{-1} cm^{-1}, respectively. In the case of **2a** and **2b** two equally intense $\pi-\pi^*$ transitions are observed. Splitting of the $\pi-\pi^*$ transitions on increasing the conjugation length was also earlier observed.[6c,15] It is also interesting to compare the ϵ-value of the d−d transition for the complexes **1a** (6740 M^{-1} cm^{-1}) and **1b** (6980 M^{-1} cm^{-1}) with that of their phenyl analogue,

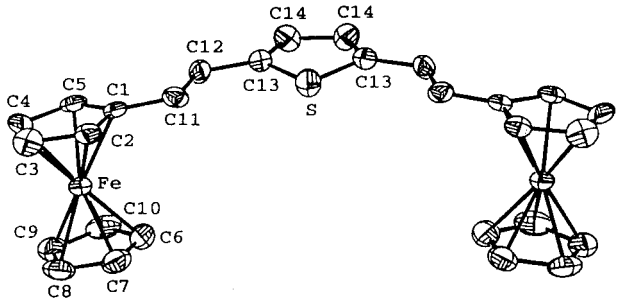


Figure 2. ORTEP plot of **1a** (40% thermal ellipsoids and hydrogen atoms omitted for clarity).

1,4-bis(β-ferrocenylvinyl)benzene (1976 M^{-1} cm^{-1}).[16] The nearly 3-fold increase in the intensity of this forbidden d−d transition in these compounds may be a result of a contribution from the charge transfer in the direction ferrocene→heteroaromatic segment facilitated by the reduced aromaticity of thiophene or furan.

The X-ray analysis of **1a** confirms the bis(ferrocenyl) structure of the complex (Figure 2). The ferrocenyl moieties have normal eclipsed conformations for the cyclopentadienyl rings. The substituted cyclopentadienyl rings are essentially coplanar with the 2,5-disubstituted thiophene nucleus. This is clearly evident from the dihedral angle between the planes passing through the thiophene and the substituted cyclopentadienyl groups (8.5(4)°). The iron−iron through-space distance is 10.894(3) Å, while the sum of the intervening bonds in the conjugation path is longer (16.684 Å). The metal−metal distance in the corresponding phenylene derivative, 1,4-bis[2-(1′,2,2′,3,3′,4,4′,4-octamethylferrocenyl)-vinyl]benzene,[5e] is 13.332(3) Å, and the sum of the bond lengths in the conjugation pathway between the two iron centers is 16.845 Å. The short through-space metal−metal distance in **1a**, when compared to 1,4-bis-(ferrocenylvinyl)benzene, should account for the weak electronic interaction identified from electrochemical studies (vide infra).

Electrochemical Studies. Cyclic voltammetry (CV) and Osteryoung square waver voltammetry (OSWV) were used to investigate the possibility of "electronic communication" between the two metal centers in the homobimetallic complexes **1**−**4**. The results of these analyses are presented in Table 2. Significant metal−metal interaction would be indicated by two distinct oxidation waves in either CV or OSWV. However, when the complexes were subjected to these two measurements, only one oxidation was observed, with the exception of **3**, for which two one-electron oxidations with a separation of 122 mV were located (Figure 3). In fact,

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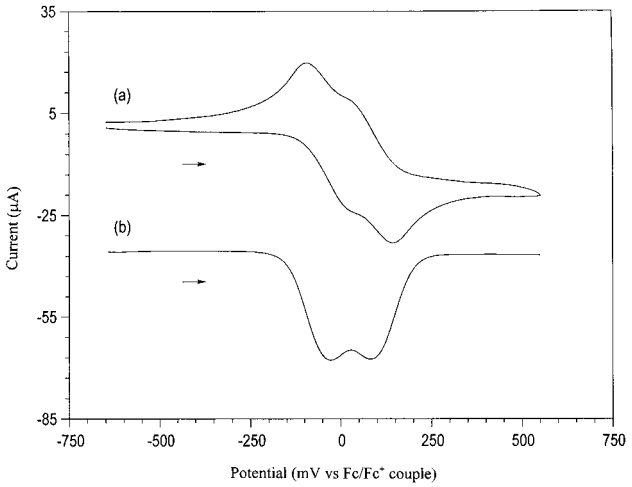

Figure 3. (a) Cyclic voltammogram and (b) OSWV of **3**.

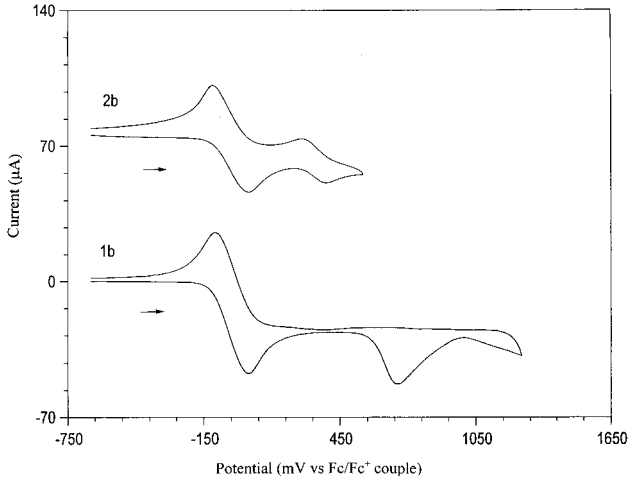

Figure 4. Cyclic voltammetric traces of the complexes **1b** and **2b** measured in dichloromethane solution (scan rate 100 mV/s).

the redox waves were considerably broadened, as noticed from the larger ΔEp values, and probably indicate two closely spaced redox waves. This means that two ferrocenyl groups weakly communicate through the less aromatic thiophene conjugation chain. An analogous phenylene-linked diferrocene species, 1,4-bis(*β*-ferrocenylvinyl)benzene, underwent a single-step two-electron oxidation with a ΔEp value similar to that of unsubstituted ferrocene.[17]

Even though the metal−metal distance in the conjugation pathway remains the same for **1a** and its phenylene analogue, the through-space metal−metal separation for **1a** is rather short (vide supra). So it is our view that the proximal disposition of ferrocenyl units in **1a** enhances the through-space electronic communication. The observation of two partially overlapping redox waves in **3** is clearly the manifestation of differences in the ferrocene environments and could not be considered as the correct measure of electronic communication between them. However, a stronger electronic communication in **3** cannot be ruled out when compared to **1** in view of its possible short through-space metal−metal distance. A small negative shift observed for the complex **2** compared to **1** can be attributed to the electron delocalization into the heteroaromatic vinyl segment. Similarly the unsaturation of the ethynyl substituent can account for the fact that the electron removal from either ethynylferrocene[18] or **4** is more difficult than from unsubstituted ferrocene. The explanation of the slightly negative shift, which occurs upon progressive insertion of thiophene units in the conjugation chain, is possibly the increased electron density in the ferrocene vicinity. This decrease in overall electronic unsaturation should stem from the electron delocalization within the central polythiophene fragments. It could facilitate the electronic communication between the ferrocenyl moieties in **4**, when compared to the analogous derivatives containing a benzenoid nucleus. This conclusion is further supported by the fact that, within a series, the peak-to-peak separation increases as the conjugation length decreases.

In addition, all the complexes display an oxidation wave at higher positive potentials attributable to the oxidation of the heteroaromatic segments, leading to the monocation radical. Formation of the heteroaromatic cation radicals is facilitated by the presence of electron-donating end groups[19] and increased conjugation chain.[20] As expected, this oxidation wave shifts negatively on increasing the conjugation chain. Interestingly, for **2b** the oxidation process associated with the furan segment is fully reversible and corresponds to a one-electron process (Figure 4). This is rather uncommon. Recent results suggest that stabilization of thienyl or furanyl cation radicals in organic compounds requires a conjugation chain comprising three or more heteroaromatic rings.[20] However, the heterobimetallics containing ferrocene and platinum or palladium *σ*-thienyl fragments exhibited a reversible one-electron oxidation process arising from the thiophene segment.[8b]

Conclusions

Soluble diferrocenyl complexes with thiophene and furan in the conjugation chain were obtained by Wittig, McMurray, and Sonogashira coupling reactions. The electrochemical studies reveal that the metal−metal interaction is weak but greater than that in the corresponding phenylene analogues. This facile synthetic methodology could be extended further to obtain nanoscale molecular wires with an increased conjugation chain. For this purpose, it is necessary to use 3,4-dialkyl thiophene segments that will increase the solubility. We are currently exploring this possibility.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, all bond distances and angles, and experimental data for X-ray diffraction studies of **1a**·CH_2Cl_2. The material is available free of charge via the Internet at http://pubs.acs.org.

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