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Polyhedron 22 (2003) 1199–1204
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A functionalized pyridinyl ligand containing binuclear biferrocene

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Received 26 November 2002; accepted 13 January 2003

Abstract

A biferrocenyl ligand containing a pyridinyl moiety which can introduce a degree of flexibility between the metal-binding domains for metallosupramolecules was prepared. The X-ray structural determination and the electrochemical measurement for this new functionalized pyridinyl biferrocene were also reported.

Keywords: Biferrocenium; Metallocene; Pyridinyl; Supramolecule

1. Introduction

Polymers containing the ferrocenyl moiety have attracted polymer and organometallic chemists for many years [1–3]. We are currently interested in the application of metallosupramolecular methodology for the synthesis of polymeric mixed-valence biferrocenium. Our basic methodology involves the use of a functionalized pyridinyl ligand containing redox biferrocene as a spacer to separate the metal-binding domains (Chart 1).

We now report a biferrocenyl ligand containing a pyridinyl moiety which can introduce a degree of flexibility between the metal-binding domains.

2. Experimental

2.1. General information

All manipulations involving air-sensitive materials were carried out by using standard Schlenk techniques under an atmosphere of N_2. Chromatography was performed on basic alumina (Merck, activity III). The solvent THF was dried and freshly distilled before use.

2.2. Preparation of 1′,1‴-dibromobiferrocene

A sample of 1′,1‴-dibromobiferrocene was prepared according to the following modified procedure [4].

Dibromoferrocene (10.32 g, 30 mmol) was placed in a freshly oven-dried three-necked flask (500 ml) and dried under vacuum at 2 mm Hg at 25 °C for 4 h. Dried THF (100 ml) followed by *n*-butyllithium (30 mmol) was added under nitrogen at −78 °C. The resulting solution was stirred at −78 °C for 1 h, during which time 1-bromo-1′-lithoferrocene gradually precipitated. Solid CuCN (1.342 g, 15 mmol) was then added, and the solution was stirred further at −78 °C for 10 min. At −78 °C, oxygen was bubbled continuously through the solution for 4 h. The solution was then stirred at room temperature for another 4 h. Water (200 ml) was added, and the mixture was then extracted with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and evaporated at reduced pressure. The residue was chromatographed on a column of alumina. Elution with hexane gave ferrocene (first band) and bromoferrocene (second band). Continued elution with hexane gave eluants which yielded the desired 1′,1‴-dibromobiferrocene (4.07 g, 51.4% yield). The compound thus prepared is

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doi:10.1016/S0277-5387(03)00108-6

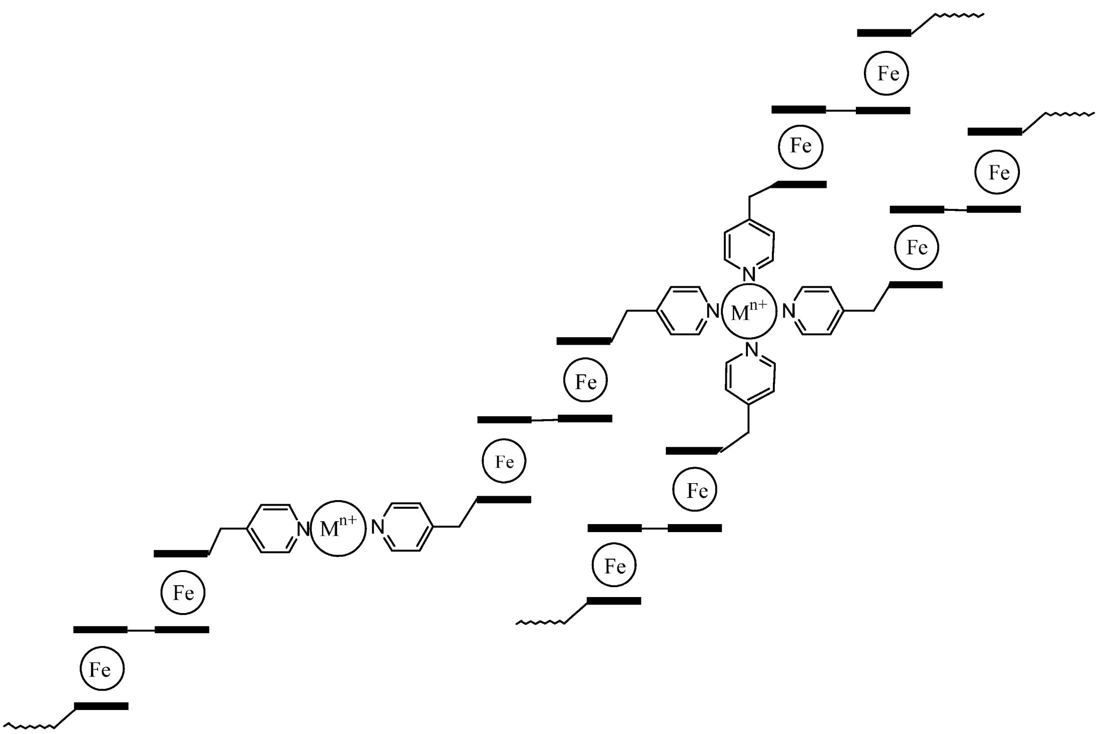


Chart 1.

pure (identification with NMR and melting point) and can be used for further reaction (Scheme 1).

2.3. Preparation of **1a–f**

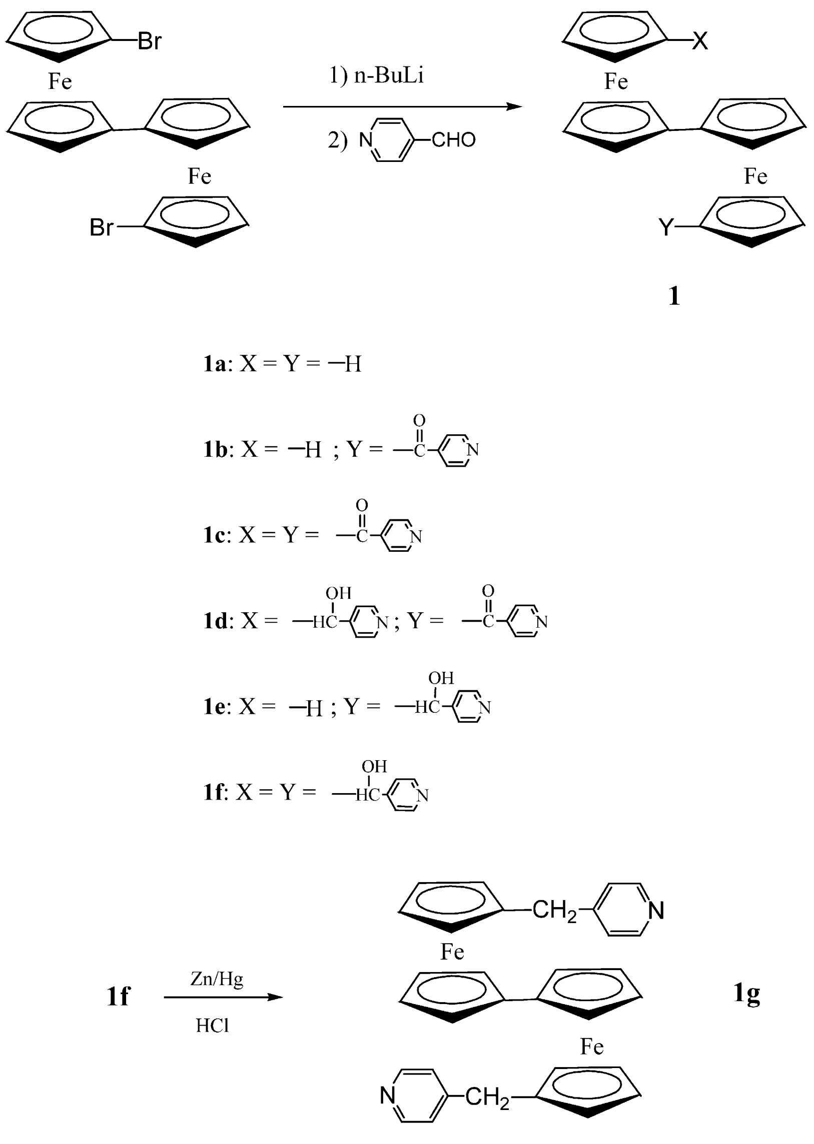
Dibromobiferrocene (5.28 g, 10 mmol) was placed in a freshly oven-dried three-necked flask (250 ml) and then dried under vacuum at 2 Torr and 30 °C for 4 h. Dried THF (60 ml), followed by *n*-butyllithium (12.5 ml; 1.6 M in hexane) was added under N_2 at −78 °C. The resulting solution was stirred at −78 °C for 1 h, during which time 1′,1‴-dilithobiferrocene gradually precipitated. The electrophilic reagent 4-pyridine carboxaldehyde (97%, 2.208 g, 20 mmol) in dried THF was then added by means of a dropping funnel over a period of 1 h at −78 °C and the solution was further stirred at room temperature for another 2 h. Water (~50 ml) was added, and the resulting mixture was extracted with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and evaporated at reduced pressure. The residue was chromatographed on a column of alumina. Elution with hexane gave eluants containing biferrocene (**1a**, 10.5% yield) identified by NMR and mass spectroscopy. Continued elution with 0.5% CH_3OH in hexane gave compound **1b** (8.5%, oil). Mass spectrum: M^+ at *m/z* 475. ^1H NMR (δ, $CDCl_3$): 3.93 (t, 5H, Cp), 4.15 (t, 2H, Cp), 4.22 (m, 4H, Cp), 4.35 (t, 2H, Cp), 4.45 (t, 2H, Cp), 4.66 (t, 2H, Cp), 7.54 (d, 2H, Py), 8.69 (d, 2H, Py). IR spectrum (KBr): C=O at 1631 cm^{-1}. *Anal.* Calcd. for $C_{26}H_{21}Fe_2NO$: C, 65.72; H, 4.45; N, 2.95. Found: C, 66.20; H, 4.39; N, 3.47.

Continued elution with 0.5% CH_3OH/hexane gave **1e** (16.3% yield) as a yellow solid (m.p. 124–125 °C). Mass spectrum: M^+ at *m/z* 477. ^1H NMR (δ, $CDCl_3$): 2.41 (br, 1H, OH), 3.98 (s, 5H, Cp), 4.03 (m, 4H, Cp), 4.23 (m, 4H, Cp), 4.39 (m, 4H, Cp), 5.16 (s, 1H, CH), 7.15 (d, 2H, Py), 8.44 (d, 2H, Py). *Anal.* Calc. for $C_{26}H_{23}Fe_2NO \cdot 1.5H_2O$: C, 61.94; H, 5.20; N, 2.78. Found: C, 62.08; H, 5.35; N, 2.53.

Continued elution with 5% CH_3OH/hexane gave **1c** (11.3% yield) as an oil. Mass spectrum: M^+ at *m/z* 580. ^1H NMR (δ, $CDCl_3$): 4.20 (t, 4H, Cp), 4.26 (t, 4H, Cp), 4.42 (t, 4H, Cp), 4.63 (t, 4H, Cp), 7.50 (d, 4H, Py), 8.68 (d, 4H, Py). IR spectrum (KBr): C=O at 1634 cm^{-1}. *Anal.* Calc. for $C_{32}H_{24}Fe_2N_2O_2H_2O$: C, 64.24; H, 4.38; N, 4.68. Found: C, 63.91; H, 4.45; N, 4.15.

Continued elution with 5% CH_3OH/hexane gave compound **1d** (9.6% yield, oil). Mass spectrum: M^+ at *m/z* 582. ^1H NMR (δ, $CDCl_3$): 2.58 (br, 1H, OH), 3.96 (d, 4H, Cp), 4.15 (d, 2H, Cp), 4.21 (d, 2H, Cp), 4.26 (d, 2H, Cp), 4.30 (t, 2H, Cp), 4.37 (t, 2H, Cp), 4.71 (t, 2H, Cp), 5.17 (s, 1H, CH), 7.16 (d, 2H, Py), 7.52 (d, 2H, Py), 8.43 (d, 2H, Py), 8.68 (d, 2H, Py). IR spectrum (KBr): C=O at 1637 cm^{-1}. *Anal.* Calc. for $C_{32}H_{26}Fe_2N_2O_2 \cdot 1.5H_2O$: C, 63.08; H, 4.80; N, 4.60. Found: C, 63.30; H, 4.45; N, 4.11.

Continued elution with 5% CH_3OH/hexane gave compound **1f** (36.6% yield) as a yellow solid (m.p. 144 °C). Mass spectrum: M^+ at *m/z* 584. ^1H NMR (δ,



Scheme 1.

$CDCl_3$): 2.88 (br, 2H, OH), 4.00 (d, 8H, Cp), 4.28 (d, 4H, Cp), 4.43 (t, 4H, Cp), 5.18 (d, 2H, CH_2), 7.16 (d, 4H, Py), 40 (d, 4H, Py). *Anal.* Calc. for $C_{32}H_{28}Fe_2N_2O_2 \cdot 2H_2O$: C, 61.96; H, 5.20; N, 4.51. Found: C, 61.89; H, 5.18; N, 4.44.

2.4. Preparation of **1g**

The reduction reaction was carried out by adding 240 ml HCl (1 M) to a mixture of compound **1f** (1.17 g, 2 mmol) and Zn/Hg in toluene under N_2. The solution was refluxed for 48 h. After cooling, sat. $NaHCO_3$ aqueous solution was added to neutralize the solution. The mixture was extracted with CH_2Cl_2. The combined extracts were dried over $MgSO_4$ and evaporated at reduced pressure. The crude product was chromatographed on a column of alumina. Elution with CH_2Cl_2 gave compound **1g** (86% yield) as a yellow solid (m.p. 105 °C dec.). Mass spectrum: M^+ at *m/z* 552. ^1H NMR (δ, $CDCl_3$): 3.33 (s, 4H, CH_2), 3.88 (t, 4H, Cp), 3.96 (t, 4H, Cp), 4.19 (t, 4H, Cp), 4.30 (t, 4H, Cp), 6.94 (d, 4H, Py), 8.39 (d, 4H, Py). *Anal.* Calc. for $C_{32}H_{28}Fe_2N_2$: C, 69.59; H, 5.11; N, 5.08. Found: C, 69.27; H, 5.12; N, 5.01.

2.5. Physical methods

^1H NMR spectra were run on a Varian INOVA-500 MHz spectrometer. Mass spectra were obtained with a VG-BLOTECH-QUATTRO 5022 system. Electrochemical measurements were carried out with a BAS 100W system. Cyclic voltammetry was performed with a glassy carbon working electrode, which was cleaned after each run. These experiments were carried out with 1×10^{-3} M solutions of biferrocene in CH_2Cl_2/CH_3CN (1:1) containing 0.1 M of $(n\text{-}C_4H_9)_4NPF_6$ as the supporting electrolyte at scan rate 100 mV s^{-1}. The potentials quoted in this work are relative to a Ag^+/Ag electrode at 25 °C.

2.6. *Structural determination of **1g***

An orange crystal ($0.20 \times 0.40 \times 0.60$ mm), which was grown by slow evaporation from a benzene solution, was used for data collection at 298 K. Cell dimensions (obtained from 25 reflections with $8.87 < 2\theta < 27.83°$) and space group data were obtained by a standard method on a Rigaku AFC7S diffractometer. The θ–2θ scan technique was used to record the intensities for all reflections for which $2\theta < 52.1°$. Absorption corrections were made with empirical Ψ rotation. Of the 2778 reflections, there were 2649 unique ($R_{\text{int}} = 0.029$). The final cycle of full-matrix least-squares refinement was based on 1242 observed reflections ($I > 3.00\sigma(I)$).

A three-dimensional Patterson synthesis was used to determine the heavy-atom positions, which phased the data sufficiently well to permit location of the remaining non-hydrogen atoms from the Fourier synthesis. All non-hydrogen atoms were refined anisotropically. During the final cycles of refinement, fixed hydrogen contributions were applied.

3. Results and discussion

3.1. *Methodology*

In the past, 1′,1‴-disubstituted biferrocenes were prepared by a coupling reaction from the corresponding 1′-substituted 1-bromoferrocene, which was prepared by the acylation of bromoferrocene in the presence of $AlCl_3$ followed by reduction [4–9]. Owing to the methodological limitation, mostly the substituents on the 1′,1‴ position in biferrocene are simple alkyl groups, halide groups or benzyl derivatives. In our previous papers [10,11], we reported a general procedure to prepare 1′-substituted 1-bromoferrocene by using 1,1′-dibromoferrocene as a precursor. In this paper, we attempted to develop an alternative method to prepare 1′,1‴-disubstituted biferrocene containing heteroatoms by using 1′,1‴-dibromobiferrocene as a precursor. The compound 1′,1‴-dibromobiferrocene was previously prepared by the direct bromination of ferrocene [12].

It is noteworthy that 1′,1‴-dibromobiferrocene is the minor product (4% yield). We found that 1′,1‴-dibromobiferrocene can be prepared easily by the direct coupling of 1,1′-dibromoferrocene, using CuCN and O_2 as the coupling reagent. The yield was maintained at 50% after work-up and recrystallization. Reaction of 1′,1‴-dibromobiferrocene with 2 equiv. of *n*-BuLi in dry THF led to 1′,1‴-dilithiobiferrocene which was treated with various electrophilic reagents without being isolated. Thus, the Cp rings in biferrocene were functionalized with various substituents.

3.2. *Solid-state structure of **1g***

Details of the X-ray crystal data collections and unit cell parameters are given in Table 1, and the molecular structure is shown in Fig. 1. Selected bond distances and angles are given in Table 2. Complete tables of positional parameters, bond distances, and bond angles are given as Supplementary material.

This neutral compound exists in a trans conformation with the two iron ions on opposite sides of the planar fulvalenide bridge observed for most biferrocenes [13]. The two Cp rings in the fulvalenide bridge are crystallograghically coplanar. Thus, the π interaction between the two ferrocenyl units is not destroyed. The average distance from the iron atom to the center of Cp rings is 1.640(1) Å. Inspection of this Fe–Cp distance shows that this value is closer to the value of 1.65 Å found for ferrocene [14] than to the value of 1.70 Å found for the ferrocenium ion [15]. The dihedral angle between the two least-squares planes of the Cp rings for a given ferrocenyl moiety is 1.52°, while the two Cp rings bonded to each iron ion are nearly eclipsed, with an average staggering angle of 9.09°. Each C–C bond length in the Cp rings agrees well with that in ferrocene (average value of 1.42 Å) [14]. The mean bond distance from the Fe atom to the ring carbon atoms is 2.033(6) Å. This value agrees well with the value of 2.045 Å observed for ferrocene.

3.3. *Electrochemical measurement*

Electrochemical data for **1a**–**1g**, as well as those for some other relevant compounds, are shown in Table 3.

Table 1
Experimental and crystal data for the X-ray structure of **1g**

Formula	$C_{32}H_{28}Fe_2N_2$
Mw	552.28
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	12.381(4)
b (Å)	8.397(4)
c (Å)	12.145(4)
β, (°)	97.12(2)
λ (Å)	0.71069
V, (Å^3)	1252.9(7)
Z	2
D_{calc} (g cm^{-3})	1.46
μ (cm^{-1})	11.81
$2\theta_{\text{limits}}$ (°)	52.1
Transaction factors	0.8321–1.0000
R	0.045
R_w	0.054

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = (\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega F_o^2)^{1/2}$.

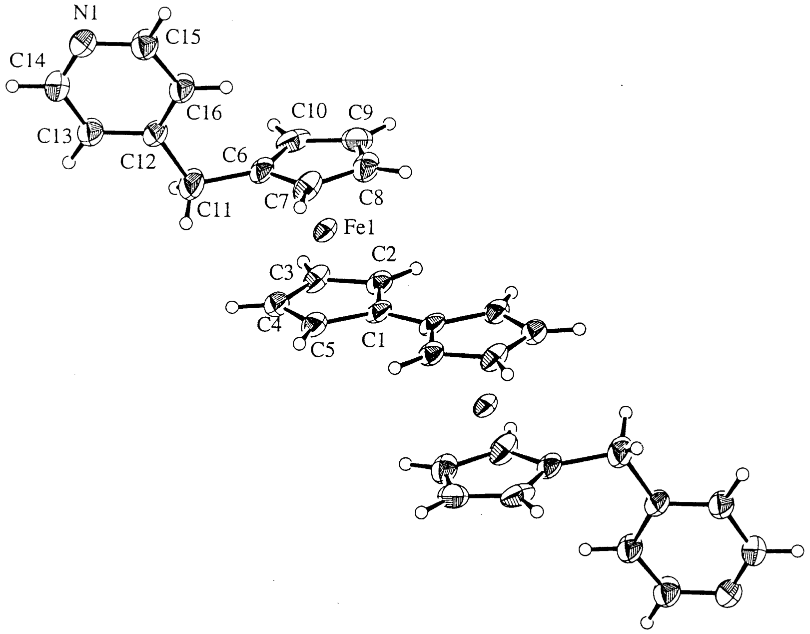


Fig. 1. Molecular view of **1g** with 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table 2
Selected bond distances (Å) and bond angles (°) of **1g**

Distance			
Fe1–C1	2.059(5)	Fe1–C2	2.046(5)
Fe1–C3	2.037(6)	Fe1–C4	2.024(7)
Fe1–C5	2.035(7)	Fe1–C6	2.024(5)
Fe1–C7	2.035(6)	Fe1–C8	2.030(7)
Fe1–C9	2.017(7)	Fe1–C10	2.024(7)
C1–C1	1.45(1)	C1–C2	1.419(8)
C1–C5	1.428(8)	C2–C3	1.423(8)
C3–C4	1.408(9)	C4–C5	1.412(9)
C6–C7	1.411(9)	C6–C10	1.43(1)
Angle			
C1–C1–C2	126.7(7)	C1–C1–C5	126.0(7)
C2–C1–C5	107.3(5)	C1–C2–C3	108.0(5)
C2–C3–C4	108.2(6)	C3–C4–C5	108.2(6)
C1–C5–C4	108.3(6)	C7–C6–C10	107.8(6)
C6–C7–C8	107.3(7)	C7–C8–C9	109.0(6)
C8–C9–C10	108.0(7)	C6–C10–C9	107.8(6)

In the case of the binuclear biferrocene **1g,** two successive reversible one-electron oxidations to yield the mono- and then the dication are observed. Electrochemical reversibility is demonstrated by the peak-to-peak separation between the resolved reduction and oxidation wave maxima and a 1:1 relationship of the cathodic and anodic peak currents (I_a/I_c in Table 3).

It has been shown [16,17] that the magnitude of the peak-to-peak separation ($\Delta E_{1/2}$) gives an indication of the interaction through the fulvalenide bridge between the two Fe sites. A comparison of the value of $\Delta E_{1/2}$ of **1g** with that of 1′,1‴-diethylbiferrocene indicates that the magnitude of interaction between the two Fe sites in these compounds is similar. However, a comparison of the $\Delta E_{1/2}$ value of **1g** with that of biferrocene indicates that the interaction between the two Fe sites in **1g** is larger than that in biferrocene.

Electrochemical measurement shows that each of the two redox waves is a one-electron-transfer process. In Eq. (1), the abbreviation [3, 3] denotes the dioxidized cation, [2, 3] the monooxidized cation, and [2, 2] the neutral compound. From the

$$[2,\ 2]+[3,\ 3] \overset{K}{\rightleftharpoons} 2[2,\ 3] \qquad (1)$$

value of $\Delta E_{1/2}$, the disproportionation equilibrium constant K (as shown in Table 3) can be calculated.

4. Conclusion

A convenient and rapid synthesis of 1′,1‴-disubstituted biferrocene containing a pyridinyl unit has been developed which allows for the preparation of metallosupramolecules.

5. Supplementary material

Tables of atomic, positional and thermal parameters, bond angles and distances. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC 182 905 for **1g**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road,

Table 3
Cyclic voltammetry for various biferrocenes

Compound	$E_{1/2}$ [a] (V)	$\Delta E_{1/2}$ [b] (V)	Δ [c] (mV)	I_a/I_c [d]	$K(\times 10^{-5})$ [e]
Ferrocene	0.41		74	1.29	
1a [f]	0.28	0.31	70	1.01	1.80
	0.59		75	1.01	
1′,1‴-diethylbiferrocene [f]	0.20	0.36	68	1.01	12.6
	0.56		70	1.02	
1b	0.48	0.54	78	1.2	14.2
	1.02 [g]		67	1.7	
1c	0.78 [h]	0.30			
	1.08 [h]				
1e	0.47 [g]	0.33	85	1.73	3.92
	0.80 [h]				
1f	0.34	0.35	66	1.37	8.6
	0.69 [g]		67	2.18	
1g	0.34	0.36	67	1.23	12.6
	0.70		66	1.11	

[a] All half-wave potentials are referred to the $Ag^+/AgCl$ electrode.
[b] Peak separation between two waves.
[c] Peak-to-peak separation between the resolved reduction and oxidation wave maxima.
[d] Peak current ratio between cathode and anode.
[e] Comproportionation equilibrium constant.
[f] From Ref. [4].
[g] Quasi-reversible.
[h] Irreversible.

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Acknowledgements

Our work was generously supported by the National Science Council (NSC90-2113-M-110-014), Taiwan, ROC, and the Department of Chemistry at Sun Yat-Sen University.

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