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Imide-bridged diferrocene for protonation-controlled regulation of electronic communication

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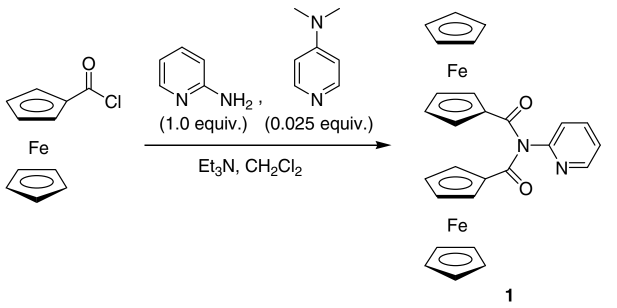
Abstract—The imide-bridged diferrocene was synthesized and characterized, permitting the protonation-controlled regulation for the electronic communication between the two ferrocenyl moieties.

Recently, there has been considerable interest in the development of switchable molecular systems.[1] Bimetallic complexes composed of redox-active transition metals and bridging spacers have received much attention as functional materials, in which electronic communication between two identical redox centers is focused on.[2] Control of the electronic communication is considered to be one of the important factors in the application to a wide variety of molecular devices.[3] The control of the electronic communication by protonation has been investigated in only some cases.[3h,j–m,p] A variety of molecules composed of multiple ferrocenyl units have been investigated due to facile organic functionalization, chemical stability, and reversible redox properties.[4] In this context, we herein report a new type of the imide-bridged diferrocene for protonation-controlled regulation of the electronic communication.

Diferrocene molecule is designed to be connected by the *N*-(pyridin-2-yl) imide bridge. *N*-(Ferrocenecarbonyl)-*N*-(pyridin-2-yl)ferrocenecarboxamide (**1**) was predominantly prepared in one step by the reaction of (chlorocarbonyl)ferrocene with 1 equiv of 2-aminopyridine in the presence of triethylamine and a catalytic amount of 4-(dimethylamino)pyridine in 79% yield according to a previous paper (Scheme 1).[5,6] The single-crystal X-ray structure determination of **1** reveals the imide-bridged structure as shown in Figure 1.[7] π-Conjugation of **1** would require the orientation of each Cp ring of the ferrocenyl moieties within a limited range of parallel to the plane of the C(ipso)–CO(bridging) bond. The steric repulsion between the ferrocenyl moieties, however, resulted in the rotation of each Cp ring away from this orientation, giving a twist conformation to set the observed β-angle, defined as the angle between the planes of the cyclopentadienyl ring and the C(ipso)–CO(bridging) bond (20.6° for C(1)–C(2)–C(3)–C(4)–C(5) and C(1)–C(51)O(1), 20.4° for C(11)–C(12)–C(13)–C(14)–C(15) and C(11)–C(52)O(2)), and dihedral angle between the planes of the C(ipso)–CO(bridging) bond and the C(51)–N(1)–C(52) bond (35.4° for C(1)–C(51)O(1) and the C(51)–N(1)–C(52), 36.0° for C(11)–C(52)O(2) and C(51)–N(1)–C(52)), in which the C(1)–C(11) distance is 3.09 Å. This conformation was also supported in solution by the ^{1}H NMR spectrum; the upfield chemical shift for the protons of the C(α) atoms of the Cp rings was observed in comparison with those of 2-pyridylferrocenecarboxamide (**2**); **1**: 4.56 ppm, **2**: 4.91 ppm. Furthermore, the dihedral angle, 58.3°, between the



Scheme 1. Preparation of the imide-bridged diferrocene **1**.

Keywords: Diferrocene; Imide bridging spacer; Electronic communication; Switching; Protonation.

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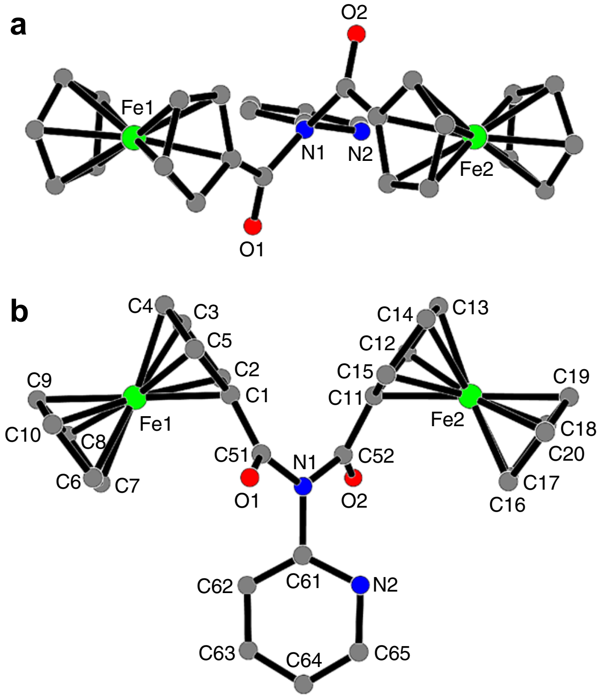

Figure 1. Molecular structure of **1** (hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): C(1)–C(51), 1.467(4); C(51)–O(1), 1.211(3); C(51)–N(1), 1.416(4); N(1)–C(61), 1.440(3); C(2)–C(1)–C(51), 127.3(3); C(5)–C(1)–C(51), 124.6(3); C(1)–C(51)–N(1), 116.0(3); C(1)–C(51)–O(1), 123.7(3); O(1)–C(51)–N(1), 120.2(3); C(51)–N(1)–C(52), 124.3(2); C(51)–N(1)–C(61), 117.7(2).

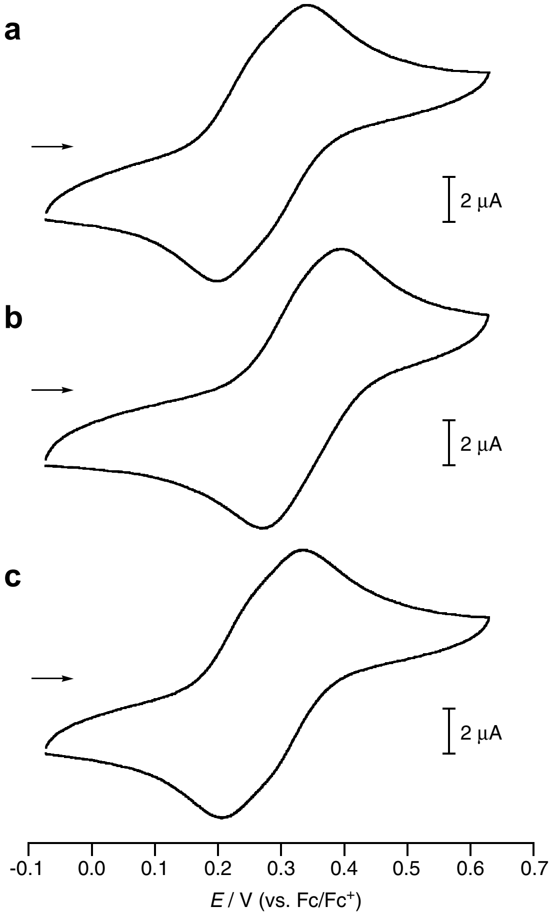

Figure 2. Cyclic voltammograms of (a) **1** in the presence of 1 equiv of DCC, (b) **1** in the presence of 1 equiv of DCC and 1 equiv of $HBF_4{\cdot}OEt_2$, and (c) after deprotonation with 1 equiv of Et_3N; in acetonitrile (5.0×10^{-4} M) containing 0.1 M Bu_4NClO_4 at a platinum working electrode with a scan rate 100 mV/s under argon.

planes of the C(51)–N(1)–C(52) bond and the pyridyl ring was observed probably due to the electronic repulsion between the lone pair of the carbonyl oxygen and the lone pair of the pyridyl nitrogen, resulting in the pyridyl ring almost perpendicular to the Cp ring (83.5° for N(2)–C(61)–C(62)–C(63)–C(64)–C(65) and C(1)–C(2)–C(3)–C(4)–C(5), 96.4° for N(2)–C(61)–C(62)–C(63)–C(64)–C(65) and C(11)–C(12)–C(13)–C(14)–C(15)). In this conformation, the upfield chemical shift for the proton of the C(62) atom was observed in the ^1H NMR spectrum.

The redox properties of **1** were investigated by cyclic voltammetry. As shown in Figure 2, the imide-bridged bisferrocene **1** in the presence of 1 equiv of *N*,*N*′-dicyclohexylcarbodiimide (DCC)[8] in acetonitrile exhibited two one-electron redox waves ($E_{1/2} = 244$ and 291 mV versus Fc/Fc^+),[9] which are assigned to the successive one-electron oxidation processes of the ferrocenyl moieties (Fig. 2a). Probably, the wave splitting could be explained by the electronic communication between the two ferrocene units. Upon addition of 1 equiv of $HBF_4{\cdot}OEt_2$ to this solution, a new slightly broad redox wave appeared at 333 mV versus Fc/Fc^+ (Fig. 2b), indicating a diminished extent of the electronic communication. The protonation associated with BF_4^- counterion might affect the interaction between the two ferrocenyl moieties. The redox wave is shifted in the anodic direction due to the increase of the electron-withdrawing nature of the imide bridging spacer by protonation. The down-field shift of the pyridyl protons was observed upon the addition of 1 equiv of $HBF_4{\cdot}OEt_2$ in the ^1H NMR spectrum of **1**, suggesting the protonation of the pyridyl nitrogen. Also, the absorbance of the ferrocenyl moieties of **1** (462 nm) was shifted to 488 nm upon the addition of 1 equiv of $HBF_4{\cdot}OEt_2$ in the UV–vis spectrum of **1**. These findings suggest the regulation of the electronic communication between the two ferrocenyl moieties by protonation. Noteworthy is that deprotonation with 1 equiv of Et_3N resulted in the original cyclic voltammogram of **1** (Fig. 2c), indicating the reversibility of the regulation of the electronic communication.

In conclusion, structural characterization of the imide-bridged diferrocene was demonstrated to provide a protonation-controlled regulation system for the electronic communication. The present fundamental system may be related to useful electrical materials.

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References and notes

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6. To a stirred mixture of 2-aminopyridine (188 mg, 2.0 mmol), 4-dimethylaminopyridine (6.1 mg, 0.05 mmol), and triethylamine (1.4 mL, 10 mmol) in dichloromethane (10 mL) was added dropwise (chlorocarbonyl)ferrocene (497 mg, 2.0 mmol) in dichloromethane (15 mL) under argon at 0 °C. The mixture was stirred at 0 °C for 7 h and then at room temperature for 17 h. The resulting mixture was diluted with dichloromethane, washed with saturated $NaHCO_3$ aqueous solution and brine, and then dried over Na_2SO_4. The solvent was evaporated in vacuo and the residue was chromatographed on a silica gel column eluting with chloroform. Ferrocene **1** or **2** was isolated by recrystallization from dichloromethane–hexane. Compound **1**: yield 79%; mp 172–173 °C (decomp.); IR (KBr) 3086, 1682, 1651, 1581, 1427 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 8.44 (ddd, 1H, $J = 4.9$, 2.0, 0.9 Hz), 7.82 (ddd, 1H, $J = 7.9$, 7.5, 2.0 Hz), 7.29 (ddd, 1H, $J = 7.5$, 4.9, 1.0 Hz), 7.26 (ddd, 1H, $J = 7.9$, 1.0, 0.9 Hz), 4.56 (t, 4H, $J = 2.0$ Hz), 4.43 (t, 4H, $J = 2.0$ Hz), 4.35 (s, 10H); ^{13}C NMR (100 MHz, CD_3CN) 176.3, 155.3, 150.0, 139.3, 123.6, 123.4, 78.1, 72.3, 71.7, 71.3 ppm; FAB-MS *m*/*z* 518 (M^+); Anal. Calcd for $C_{27}H_{22}N_2O_2Fe_2$: C, 62.58; H, 4.28; N, 5.41. Found: C, 62.49; H, 4.44; N, 5.41. Compound **2**: yield 6%; mp 126–128 °C (decomp.); IR (KBr) 3394, 3078, 1658, 1574, 1520, 1435 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 8.42 (br, 1H), 8.32 (ddd, 1H, $J = 4.9$, 1.9, 0.9 Hz), 8.21 (ddd, 1H, $J = 8.4$, 1.0, 0.9 Hz), 7.77 (ddd, 1H, $J = 8.4$, 7.4, 1.9 Hz), 7.09 (ddd, 1H, $J = 7.4$, 4.9, 1.0 Hz), 4.91 (t, 2H, $J = 1.9$ Hz), 4.47 (t, 2H, $J = 1.9$ Hz), 4.24 (s, 5H); ^{13}C NMR (100 MHz, CD_3CN) 169.0, 152.1, 148.2, 138.1, 119.4, 113.9, 75.7, 71.2, 69.8, 68.7 ppm; FAB-MS *m*/*z* 306 (M^+); Anal. Calcd for $C_{16}H_{14}N_2OFe$: C, 62.77; H, 4.61; N, 9.15. Found: C, 62.65; H, 4.93; N, 8.79.
7. Crystal data for **1**: $C_{27}H_{22}N_2O_2Fe_2$, $M = 518.18$, triclinic, space group $P1$ (no. 2), $a = 10.729(1)$ Å, $b = 11.893(2)$ Å, $c = 10.429(1)$ Å, $\alpha = 115.994(8)°$, $\beta = 90.01(1)°$, $\gamma = 111.550(9)°$, $V = 1091.8(3)$ Å^3, $Z = 2$, $T = 23.0$ °C, $D_{calc} = 1.576$ g cm^{-3}, $\mu(MoK\alpha) = 13.56$ cm^{-1}, Mo Kα radiation ($\lambda = 0.71069$ Å), $R = 0.037$, $Rw = 0.030$. Crystallographic data (excluding structure factors) for the structure reported in this Letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-640891 for **1**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44 1223/336 033; e-mail: deposit@ccdc.cam.ac.uk].
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